

CONVERSION OF PETROLEUM

PRODUCTION OF MOTOR FUELS
BY THERMAL AND CATALYTIC
PROCESSES

BY

A. N. SACHANEN, D.Sc.

RESEARCH AND DEVELOPMENT DIVISION,
SOCONY-VACUUM OIL CO., INC.

BOOK DEPARTMENT

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Dedicated to my wife
ELIZABETH V. SACHANEN

Preface

This book relates to the fundamental principles and practices of converting petroleum products into gasoline and other fuels.

At the present time the conversion of petroleum can be carried out by various methods, including thermal and catalytic cracking, hydrogenation, polymerization and alkylation. Unquestionably thermal cracking retains its position and remains thus far the most important process among the aforementioned methods of conversion. On the other hand, the part played by the other methods becomes of more and more importance, particularly in the production of high-octane fuels. The catalytic character of the other methods of conversion is emphasized in the title.

The author has realized the difficulties encountered in covering the broad problem of the conversion of petroleum in one volume and has therefore been confronted with limiting the scope of the book. A complete survey of the enormous literature on the subject in one volume of conventional size seems to be prohibitive. Therefore only the most important works, from the point of view of the author, have been referred to and discussed. The historical development of the conversion of petroleum is beyond the scope of the present book. As a consequence, many articles of an important historical value have not been included.

Consideration of patents has been deliberately omitted. The patent literature on the conversion of petroleum is too voluminous to be presented in this book. In addition, a critical survey and digest of the patent literature are almost prohibitive for many reasons. A non-critical survey would give quite a wrong conception of the value claimed for numerous inoperative patented processes and methods. As a rule, the technical and scientific literature has been preferred to patent disclosures. The patent literature has been used in a few cases, in which other materials were not available.

The author has had no connection with the development of the Houdry processes referred to in subsequent pages, and the opinions expressed in this book regarding them are his own.

The author wishes to thank Mr. V. A. Kalichevsky for helpful suggestions and Dr. J. B. Rather, in charge of the General Laboratories of Socony-Vacuum Oil Company, Inc., for permission to publish this book. The author is also indebted to the Foster Wheeler Corporation, the *Oil and Gas Journal*, the *National Petroleum News*, the *Refiner* and others for their courtesy in supplying various materials, flow-sheets and diagrams.

A. N. SACHANEN.

Woodbury, New Jersey, February, 1940

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Chapter 1

Thermal and Catalytic Reactions of Hydrocarbons

CHEMICAL COMPOSITION OF CRACKING STOCKS*

Cracking stocks consist essentially of hydrocarbons of the following classes: paraffins, naphthenes, and unsaturated and aromatic hydrocarbons. Various combinations of these main classes frequently occur in cracking stocks, as well as in all petroleum products. The naphthenes and aromatics, for instance, usually contain more or less long paraffinic side chains; or the naphthenic and aromatic rings are frequently combined in one molecule forming a naphtheno-aromatic hydrocarbon.

The unsaturated hydrocarbons are almost entirely absent in straight-run products, but they are easily formed in the first stages of cracking and play an important part in all cracking reactions. The unsaturated hydrocarbons formed in cracking belong mostly to straight-chain monoölefins, cycloölefins and diolefins being of secondary importance. Other classes of unsaturated hydrocarbons, such as the derivatives of acetylene, terpenes, etc., do not occur in cracking stocks to any appreciable extent.

Of the naphthenes present, the derivatives of cyclopentane and cyclohexane are predominant in low-boiling petroleum products, but the existence of other naphthenes cannot be considered as proved. The polynuclear naphthenes and aromatics, as well as the combined naphtheno-aromatics, are widely distributed in high-boiling fractions of petroleum products.

Only in exceptional cases do the petroleum products to be cracked consist of the hydrocarbons of the same class, as, for example, oil field gases containing only paraffin hydrocarbons. Refinery gases include paraffins and olefins. Straight-run liquid products consist of paraffins, naphthenes and aromatics in various proportions depending on the nature and the boiling range of the product. Table 1 gives a broad idea of the proportions of different hydrocarbons in straight-run petroleum products.¹¹⁷

The data of Table 1 show that the content of paraffins decreases and that of aromatics increases with increasing boiling range of petroleum products. It is to be noted that the classification of hydrocarbons in Table 1 is conventional, *i.e.*, the paraffins are understood as open-chain saturated hydrocarbons; the aromatics as hydrocarbons possessing "aromatic" properties, first of all, the property to react with concentrated sulphuric acid with formation of sulphonic acids; and the naphthenes as cyclic hydrocarbons of non-aromatic properties.

*By the term "cracking" is meant all processes of thermal and catalytic conversion of petroleum.

CONVERSION OF PETROLEUM

Table 1. Chemical Composition of Petroleum Fractions.

Fraction	Boiling Range, 50% A.S.T.M. Distillation (°F.)	—Paraffin Base Crude— (% by Weight)			—Asphaltic Base Crude— (% by Weight)			
		Paraf.	Naphth.	Arom.	Paraf.	Naphth.	Arom.	Unsat.
Gasoline	280	65	30	5	35	55	10	..
Kerosene	450	60	30	10	25	50	25	..
Gas oil	600	35	55	15	..	65	33	2
Heavy dist.	750	20	65	15	..	55	43	2

To avoid a certain indefiniteness of the conventional classification, Waterman and his associates proposed another criterion of the classification of hydrocarbons.¹³⁶ They expressed the chemical composition of petroleum products by the weight percentage of paraffinic side chains (including paraffinic hydrocarbons), and aromatic and naphthenic rings that are assumed to consist of six carbon atoms. Table 2 gives the chemi-

Table 2. Chemical Composition of Petroleum Fractions (Content of Paraffinic Side Chains, Naphthenic and Aromatic Rings).

Fraction	Boiling Range, 50% A.S.T.M. Distillation, (°F.)	—Paraffin Base Crude— (% by Weight)			- Asphaltic Base Crude - (% by Weight)		
		Paraf. Side Chains	Naphth. Rings	Arom. Rings	Paraf. Side Chains	Naphth. Rings	Arom. Rings
Gasoline	280	77	20	3	57	37	6
Kerosene	450	76	18	6	48	36	16
Gas oil	600	75	17	8	46	31	23
Heavy dist.	750	76	16	8	44	29	27

cal composition of the same petroleum distillates in the terms of the "ring analysis."

In addition to the hydrocarbons, cracking stocks may contain oxygen, sulphur and nitrogen compounds, including naphthenic and other acids, various sulphur compounds, oxygen containing neutral resins and asphaltenes, and nitrogen organic bases. The relative amount of all these compounds does not exceed customarily 0.5-1.0 per cent in the low-boiling fractions, including gas oils, but may be as high as 10 per cent and more in the residues produced from heavy asphaltic crudes. Very little is known of the behavior of the oxygen and sulphur compounds at temperatures of cracking, and the following discussion concerns mostly the reactions of the aforementioned classes of hydrocarbons.

The cracking and other reactions of hydrocarbons are interpreted from the thermodynamic standpoint. The author did not apply the theory of free radicals to the interpretation of cracking phenomena.

By postulating the occurrence of certain free radicals, and by other more or less arbitrary assumptions, one may develop an apparently satisfactory representation of the decomposition reactions of hydrocarbons. Actually this method scarcely gives anything beyond the arbitrary assumptions involved. With somewhat modified assumptions the usual chemical equations would give the same picture. Even for such a comparatively simple reaction as the thermal decomposition of ethane, the "molecular" representation of the experimental results seems to be even

more adequate¹²⁵ than that postulated on the basis of the theory of free radicals.¹⁰⁹

Thus it is possible that the decomposition of hydrocarbons takes place partly by the chain reactions of radicals postulated by Rice, and partly by direct splitting into new molecules of lower molecular weight. The molecular or radical mechanism of the decomposition may be very complex, particularly for high molecular weight hydrocarbons and under high pressures.

The author would not like to deny or minimize a probable occurrence of free radicals and their part in the decomposition of hydrocarbons, but he does not believe that the theory in its present state may be successfully applied to the cracking phenomena.

PARAFFIN HYDROCARBONS

Free Energy of Paraffin Hydrocarbons

The paraffin hydrocarbons in charging stocks for cracking are of a very large range of molecular weight, from methane to solid paraffins containing 25 and more carbon atoms in a molecule. Methane is beyond the scope of this book due to its exceptional thermal stability. The temperatures which must be used for the thermal conversion of methane (1000°C. and more) are far beyond the temperature range of the most severe cracking conditions. All other paraffins, particularly those containing four or more carbon atoms, play an important part in the cracking reactions. As will be shown in the next paragraphs, the paraffinic side chains of naphthenes and aromatics undergo the same decomposition reactions as the paraffin hydrocarbons.

According to the latest data of Thomas, Egloff and Morrell,¹³⁴ the free energy of formation of normal paraffin hydrocarbons in the gaseous state may be expressed by the following linear equation:

$$\Delta F^\circ = -10,550 - 5,890n + 25.2nT - 2.2T \quad (1)$$

in which n represents the number of carbon atoms, T the absolute temperature and ΔF° the free energy of formation at a pressure of one atmosphere for all substances involved. This equation gives very satisfactory results for any of the hydrocarbons above methane for the temperature range up to 700°C.

It is probable that the free energy of formation of branched paraffins is slightly more positive in comparison with normal hydrocarbons. According to Francis,³⁴ the increment of ΔF° of a branched paraffin over a normal hydrocarbon having the same number of carbon atoms equals

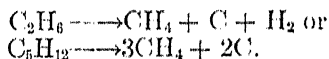
$$4.5rT - 740r, \quad (2)$$

where r is the number of branches. However, according to the calculations of Ewell,^{29a} the branched chain paraffins are more stable at low

temperatures up to 150-175°C. In the temperature range of 150-175°C. all isomers of paraffins have approximately the same value of free energy. At higher temperatures the straight-chain paraffins become more stable than their isomers.¹⁵¹ It should be emphasized that the difference in the values of free energy ΔF° for various isomers is not very substantial according to equation (2). For instance, ΔF° of formation of normal octane at 500°C. is calculated to be +96,300 cal. and that of trimethylpentane +104,500 cal., the values being of the same order.

The calculation of ΔF° for any hydrocarbon from ethane for 400-500°C. (752-932°F.) and higher shows that the values ΔF° are positive at these temperatures. It means that at cracking temperatures all paraffins, with the exception of methane, are unstable with respect to carbon and hydrogen, or, in other words, that the decomposition of paraffins into elements is thermodynamically probable under cracking conditions.

The decomposition of paraffins into methane and elements also is thermodynamically probable, as, for instance, the reactions:



The free energies ΔF° of these reactions may be represented respectively by the following equations:

$$\begin{aligned} \Delta F^\circ &= 2,400 - 24.7T', \\ \Delta F^\circ &= -15,000 - 60.3T' \end{aligned}$$

According to the first equation, the values of ΔF° of the first reaction are negative for the temperatures higher than 97°F., i.e., for the whole range of cracking temperatures. The free energy of the second reaction is negative at any temperature.

Similar results may be obtained for the decomposition of paraffins of high molecular weight into ethane and elements, or methane, ethane and elements.

The rate of all these reactions, leading to the formation of elements or low molecular weight paraffins and elements, however, is extremely slow under the conditions of cracking. It is a well-known fact that paraffin hydrocarbons of various molecular weights can be extensively cracked at temperatures of 400 to 600°C. (752 to 1112°F.) without any appreciable coke formation. The coke formation starts only in the advanced stages of cracking, as a result of some secondary reactions to be discussed in the following paragraphs.

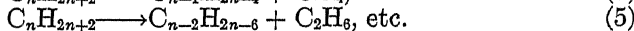
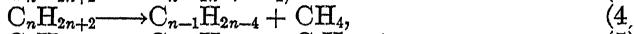
The reactions of the decomposition into elements may be practically possible to a certain extent either at very high temperatures above 700°C. (1292°F.), or in the presence of certain metallic catalysts under more moderate temperature conditions. Nickel is one of the most powerful catalysts, accelerating the decomposition of paraffins, as well as other hydrocarbons, into elements or into methane and elements. Sabatier and

Senderens¹¹¹ demonstrated a slight decomposition of methane into carbon and hydrogen at 390°C. (734°F.) and of ethane at 325°C. (617°F.) in the presence of nickel. Frey and Smith³⁹ and Hurd⁵⁶ observed a very rapid decomposition of propane and butane into carbon and gases at 350-400°C. (662-752°F.) and 500°C. (932°F.) respectively in the presence of the same catalyst. Other catalysts of the same type are: copper, iron, Monel metal, many other heavy metals and certain non-metals, such as selenium. The powdered metals are particularly active. On the other hand, the fact that iron tubes do not catalyze the elemental decomposition of oils in the conventional cracking is due either to the inactivity of iron in massive form or to the deactivation of the metallic surface by the deposition of carbon. However, the catalytic action of the metallic surface of tubes may be appreciable at the higher temperatures used in vapor-phase cracking or in such processes as dehydrogenation. The pretreatment of tubes with steam or hydrogen sulphide at high temperatures may deactivate the metallic surface. A small quantity of steam or hydrogen sulphide (or other sulphur compounds) added to the charging stock may produce the same effect. As a result of such a treatment, the active metallic surface is covered with inactive oxides or sulphides. The effect obtained may also be attributed to poisoning of the active surface by oxides or sulphides formed.

The catalytic reactions of the total decomposition of gaseous paraffins may have a certain practical value for the production of hydrogen and carbon black. The non-catalytic decomposition of methane into elements rapidly proceeds at temperatures of 1100 to 1200°C. producing high yields of carbon black up to 50 per cent and more of the theoretical yield. The reaction time is 1-2 seconds. The carbon black produced is inferior to that obtained by the Channel process.

Free Energy of Decomposition of Paraffins

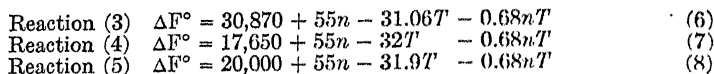
The second class of monomolecular decomposition reactions of paraffins leads to the formation of olefins. Various types of these reactions are theoretically possible, according to the following general equations:



The first of these reactions is the dehydrogenation of a paraffin forming an olefin of the same number of carbon atoms and hydrogen. In other reactions the scission takes place more to the middle of the molecule of paraffin. As a result, methane or other paraffins are formed, depending on the point of scission, as well as olefins having a smaller number of carbon atoms. In the following discussion the reaction of the scission or break-down of carbon-carbon bonds will be specified as the splitting decomposition.

On the basis of general equations for normal paraffins (1), normal

olefins (13) and methane,⁹⁹ the following equations for the reactions of cracking of normal paraffins have been calculated:



It should be noticed that equations (7) and (8), as well as those of other similar reactions forming various paraffins and olefins, are practically identical.

If the small difference in the free energy of reactions (4) and (5) may be considered as significant, the conclusion should be drawn that methane-splitting (4) is more probable than other reactions of decomposition. On the contrary, de-ethenization is the least probable reaction. Schultz^{118b} assumes accordingly that, of the two molecules formed by splitting, the olefin would be larger than the paraffin. The kinetics of cracking, however, does not follow such small differences in the free energy of various splitting reactions. As will be seen later, the formation of methane is not a predominant decomposition in cracking hydrocarbons. The cleavage takes place at various carbon-carbon bonds but predominantly in the middle of the molecule, particularly in the case of high molecular weight hydrocarbons.

According to Parks and Todd,¹⁰⁰ ΔF° for the decomposition of iso-octane into isobutane and isobutene may be represented as follows:

$$\Delta F^\circ = 18,350 - 39.1T. \quad (9)$$

This equation as compared with the corresponding equation for normal butane

$$\Delta F^\circ = 20,450 - 36T, \quad (10)$$

shows that the splitting decomposition of normal and iso-paraffins is expressed by very close equations.

The following important conclusions may be drawn from ΔF° equations (6), (7) and (8).

1. For the same reaction of cracking and at the same temperature, the free energies of decomposition, ΔF° , of paraffins are more negative for paraffins of high molecular weight (*i.e.*, greater number n). The thermal stability of paraffins decreases with increasing molecular weight. The same conclusion is valid for other classes of petroleum hydrocarbons, and, thus, heavier fractions of petroleum products are less stable and are cracked more easily than lighter ones, in accordance with the experimental data, discussed in Chapter 2.

2. Other conditions being equal (number of carbon atoms and temperature), the free energy of dehydrogenation of a paraffin is much more positive than that of splitting decomposition. Zero value of ΔF° of the dehydrogenation of normal butane, for example, corresponds to 647°C. whereas that of the splitting decomposition with formation of methane or ethane corresponds to a much lower temperature, 313°C. Thus, from

the thermodynamic standpoint, the dehydrogenation of paraffins is a less probable reaction than the splitting decomposition forming a paraffin and an olefin. The breakdown of the paraffin molecules should take place more easily between two carbon atoms.

3. Free energies, ΔF° , of the splitting decomposition of paraffins to an olefin of a lesser C-number and a paraffin are approximately independent of the C-number of the olefin formed. Thus, the probability of the breakdown of paraffin molecules is about the same for any two neighboring carbon atoms independently of their position in the molecule.

4. The relative thermal stability of various paraffins may be represented by the temperatures corresponding to the zero values of the free energy of different decompositions calculated by equations (6) and (8). These data are given in Table 3. They clearly show an increasing thermal instability of paraffins with increasing molecular weight and a greater probability of the splitting reactions over dehydrogenation.

Table 3. Temperatures Corresponding to Zero Values of Free Energy.

Hydrocarbon	Dehydrogenation	Splitting Decomposition
Ethane	787°C. (1448°F.)	...
<i>n</i> -Butane	647°C. (1196°F.)	313°C. (599°F.)
<i>n</i> -Decane	556°C. (1033°F.)	259°C. (498°F.)
<i>n</i> -Eicosane	444°C. (831°F.)	192°C. (378°F.)

Dehydrogenation of Paraffins

There is a very large amount of experimental material concerning the cracking of low molecular weight paraffins, including pentanes and hexanes. Much less has been done for high molecular weight paraffins.

The reactions of paraffins in the first stages of cracking, or primary reactions, are the most important of the characteristics of paraffins. In the advanced steps of the process many secondary reactions occur involving olefins formed as a result of the primary reactions. The method of extrapolation of the results of cracking to zero per cent decomposed may be of value for the investigation of the primary reactions.⁴⁰

Dehydrogenation of paraffins in cracking takes place usually to a much lesser extent than splitting decompositions, particularly for high molecular weight paraffins. The experimental results are in satisfactory qualitative agreement with the above thermodynamic conclusions.

The process of dehydrogenation of low molecular weight paraffins, particularly of gaseous hydrocarbons, has undoubtedly a commercial future due to the transformation of low-priced gaseous paraffins into valuable olefins. In comparison with splitting decomposition, dehydrogenation of paraffins produces very high yields of olefins, theoretically as high as 95-96 per cent for such hydrocarbons as propane or butanes. The average yield of olefins in the splitting reactions should be close to 50 per cent.

The simplest example of dehydrogenation is that of ethane, which was studied by Pease and Durgan.¹⁰⁵ Ethane was dehydrogenated non-catalytically to ethene and hydrogen at temperatures of 600 to 700°C.

and at pressures of 0.55-1.05 atm. Under these conditions the reaction is reversible, and the equilibrium was approached from both sides.

In the presence of certain catalysts, however, the dehydrogenation of some heavier paraffins may also be a predominant reaction. Frey and Huppke³⁸ found that propane and butanes were dehydrogenated at temperatures of 350 to 500°C. at atmospheric pressure in the presence of a chromic oxide gel. The products of the reaction consisted mostly of hydrogen and an olefin of the same number of carbon atoms. Normal butane yields normal butenes and isobutane, isobutenes.

According to Dunstan and Howes,²⁰ oxides of molybdenum, zinc and magnesium, chromic oxide on silica gel, titania on charcoal, oxides of nickel, aluminum, zinc on charcoal, manganese oxide on charcoal, copper or alumina on charcoal, and active charcoal itself are catalysts for the dehydrogenation of normal butane in certain limits of temperature, depending on the nature of catalysts. Oxides of molybdenum-zinc-magnesium, for instance, are active between 400 and 475°C., and alumina on charcoal is active between 525 and 650°C. The allowable throughput of butanes over the above-mentioned catalysts at temperatures of 400 to 600°C. is from 250 to 2000 volumes per volume of catalyst per hour, depending on the activity of catalysts.

Burgin, Groll and Roberts¹⁴ report that activated carbon and activated alumina possess great dehydrogenating activity for paraffin hydrocarbons at high temperatures. The presence of small amounts of water or hydrogen sulphide is essential for the activity of the catalysts. The temperature used in a continuous process for the dehydrogenation of propane and butanes is from 550 to 650°C. The activity of alumina may be appreciably increased by the incorporation of more active catalysts, such as chromium oxide or ferric oxide. When activated alumina was used as a catalyst, isobutane was converted to isobutene at 600°C. to the extent of 36.2 per cent. The percentage of the conversion was increased to 37-38 at a lower temperature (550°C.) when chromic or ferric oxide was impregnated in the catalyst.

Some secondary reactions take place in the process described, resulting in the formation of coke and in the deterioration of the catalyst. Restoration of the original activity of catalysts can be accomplished by oxidation with a stream of air at a temperature of 600-700°C.

Grosse and Ipatieff^{49a} dehydrogenated paraffins to olefins under similar conditions. The process was performed at temperatures of 500 to 575°C. and at atmospheric pressure in the presence of catalysts, consisting of oxides of chromium, vanadium, titanium, etc., supported on activated alumina. Under these conditions the dehydrogenation is largely predominant. Ethane was converted into ethene, propane into propene and butanes into butenes, giving a 90-95 per cent of the theoretical yield.

The thermal dehydrogenation of paraffins cannot be carried out successfully due to the predominance of the splitting reactions, as will be seen in the next section. The thermal dehydrogenation of iso-paraffins,

for instance iso-butane, may give better yields of olefins with the same number of C-atoms. As will be shown later, the thermal decomposition of iso-paraffins produces higher yields of dehydrogenated hydrocarbons of the same framework.

In general the dehydrogenation of paraffins, even in the presence of catalysts, is accompanied by splitting reactions and only in rare cases can it be performed more or less selectively. In distinct contrast to this, the non-destructive dehydrogenation of some naphthenes is feasible, as will be seen later in this chapter. This difference is due to the low temperature of the catalytic dehydrogenation of naphthenes, not exceeding 300°C., under which conditions the splitting reactions do not occur to any appreciable extent.

Dehydrogenation of paraffins is carried out in recycle operation to avoid too high yields of olefins per pass resulting in various secondary reactions. Nash and Howes^{88b} give the following maximum extent of dehydrogenation per pass:

Ethane	9.5 per cent	
Propane	28.2	" "
<i>n</i> -Butane	52.3	" "
Isobutane	60.0	" " (approx.)

In practice, on the C₃-C₄ paraffin fraction the decomposition per pass does not exceed 38 per cent. In commercial practice in this country the yield of butenes and other olefins is usually limited to 20-25 per cent per pass.

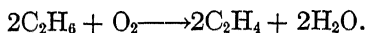
In the latest publication Grosse and his associates^{49b} give more details on the catalytic dehydrogenation of butanes over chromic oxide on alumina. The conditions and results of the process may be summarized as follows:

Temperature, from 525 to 580°C. (976 to 1075°F.); pressure (outlet), from 5 to 20 pounds per sq. inch; space velocity, about 1,400 per hour; length of cycle, about 1 hour; total conversion (mol C₄H₁₀ converted per 100 mols charged), from 24.9 to 31.6 per cent; yield of C₄H₈ (mol C₄H₈ per 100 mols C₄H₁₀ charged), from 21.8 to 28.2.

These data show that the dehydrogenation of butanes to butenes is a predominant process. The side reactions do not exceed, on an average, 10 per cent of the total conversion. The catalyst may be reactivated by oxidation.

The use of such catalysts as alumina or chromic oxide at high temperatures as dehydrogenation catalysts is of interest from the theoretical standpoint. It is known that these oxides do not catalyze hydrogenation and dehydrogenation reactions at low temperatures. The influence of temperature on the adsorption properties and catalytic activity of the catalysts will be discussed in Chapter 3.

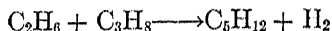
Another method of dehydrogenating paraffins is a reaction with oxygen or air, for instance according to the equation:



The free energy of this reaction is strongly negative at temperatures about 500°C. (932°F.).

The partial dehydrogenation of paraffins by oxygen takes place at temperatures of about 600-700°C. The reaction is accompanied by many secondary and side reactions, including the formation of methane, liquid products and coke. No commercial application of this reaction is known due to the difficulties encountered in the controlled oxidation of paraffins to olefins.

Bimolecular dehydrogenation of paraffins with formation of a high molecular paraffin, *e.g.*, according to the following equation



is thermodynamically impossible. The free energy ΔF° of the reactions of this type is strongly positive at any temperature, as can be seen from the following equation relating to the above reaction:

$$\Delta F^\circ = 8,400 + 6.3T$$

This proves that the formation of olefins is a prerequisite of the conversion of gaseous paraffins into high molecular paraffins and other hydrocarbons.

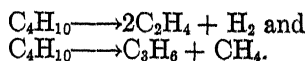
Splitting Decomposition of Paraffins

As has been stated above, the splitting decomposition of paraffins predominates in thermal cracking in the absence of catalysts, and dehydrogenation takes place to a comparatively small extent. There are very reliable and compatible data on the thermal cracking of normal butane under low pressures, obtained by different investigators. The general results of these investigations are summarized in Table 4. The data of Frey and Hepp or Hurd and Spence supported by the latest data of Steacie and Puddington^{124b} seem to be the most accurate.

A comparatively satisfactory agreement between the results of different authors should be mentioned.

The data of Table 4 show the predominance and approximately equal magnitude of two reactions of splitting decomposition possible for *n*-butane. The time of cracking in these experiments was from 24-30 seconds at 600°C., corresponding to 20 per cent of conversion, to 18-20 seconds at 700°C., corresponding to 75 per cent of conversion.

The primary decomposition reactions of butane given above take place at temperatures up to 700°C. At higher temperatures the decomposition shifts to dehydrogenation and demethanation. Cambron^{15a} investigated the decomposition of butane at 962°C. and found that the following reactions predominate:



In the thermal cracking of iso-butane, dehydrogenation plays a much more important part than in the case of normal butane. According to

Table 4. Thermal Cracking of *n*-Butane.

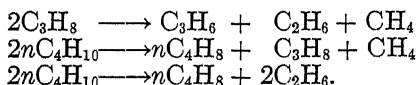
Temperature (°C.)	100 Moles of Cracked <i>n</i> -Butane Form:			Reference
	CH ₄ + C ₃ H ₆	C ₂ H ₆ + C ₂ H ₄	C ₄ H ₈ + H ₂	
575	60	30	10	Frey and Hepp ³⁶
600	55	40	5	Hurd and Spence ⁶⁰
600	48.5	34.5	16	Neuhaus and
650	48	37.7	12.3	Marek ^{92a}
700	35	40	20	Hague and Wheeler ⁵
700	44	46	5	Hurd and Spence ⁶⁰
700	54	29*	15	Schultze <i>et al.</i> ¹²⁰

* This figure includes also the reaction forming 2C₂H₄ + H₂, accepted by the authors.

Hurd and Spence,⁶⁰ Pease,¹⁰² Frey and Hepp,³⁶ Marek and Neuhaus,⁹³ and Schultze and Weller,¹²⁰ the dehydrogenation of iso-butane to iso-butene and hydrogen is of about the same magnitude as the splitting decomposition to propene and methane, or possibly even greater. Marek and Neuhaus calculated by the method of extrapolation to zero time that at 600-650°C. the primary decomposition of iso-butane produces 63 moles per cent of iso-butene and hydrogen and 34.5-36 mole per cent of propene and methane. Schultze and Weller found that at 700°C. the primary cracking of iso-butane gives 52 mole per cent of dehydrogenation and 48 per cent of splitting decomposition.

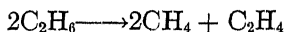
Egloff, Thomas and Linn²⁸ studied the effect of pressure on the decomposition of butanes and propane. They found that the rate of decomposition of these hydrocarbons into an olefin and a paraffin is almost independent of the pressure (from 1 to 7 kg./cm²). On the contrary, the dehydrogenation of iso-butene is strongly suppressed by the increase in pressure. These results are in evident agreement with the reversibility of dehydrogenation reactions of simple paraffins and the virtual irreversibility of splitting decompositions.

Only monomolecular reactions of the splitting decomposition of paraffins were discussed in the previous paragraphs. Some investigators, however, accept the occurrence of the bimolecular reactions, as for example



For instance, Tropsch, Thomas and Egloff¹³⁵ studied the cracking of normal butane at 525 and 550°C. and 50 kg. per sq. cm. pressure, and found a considerable formation of normal butene, which could not be accounted for on the basis of dehydrogenation. The extent of the dehydrogenation and the formation of hydrogen were very small. The last two reactions may explain the formation of normal butene as a result of the bimolecular reactions of decomposition.

Dintzes and his collaborators^{18a} have also found that the bimolecular reaction of the decomposition of ethane



increases with increasing pressure from 1 to 26 atmospheres at 635°C.

It is well known that the decomposition reactions are mostly monomolecular, and that the probability of bi- and polymolecular reactions is small, at least under low pressures. The high pressures of commercial cracking, however, are in favor of bimolecular reactions, and therefore the possibility of such reactions should not be overlooked, particularly for low molecular weight paraffins and high pressures.

It would take too much space to discuss in detail the experimental results of the cracking of higher paraffins. Thermal decomposition of such paraffins as pentanes or hexanes leads to the formation of various olefins and paraffins of lower molecular weight. Practically all the carbon-carbon bonds are broken during the cracking. The conclusions of some authors⁵⁰ on the preponderance of methane splitting reactions seem to be in disagreement with the majority of experimental results. Dehydrogenation, leading to the formation of an olefin of the same C-number and hydrogen, occurs to a smaller extent in comparison with the splitting reactions, particularly for hydrocarbons of normal structure.

The cracking of high molecular weight paraffins, present in common cracking stocks, gives very interesting results which will be briefly discussed. The most detailed study of the cracking of *n*-decane, *n*-dodecane, *n*-hexadecane, isohexadecane (1,8-dimethyltetradecane), and dotriacontane was made by Tilicheyev and Feigin¹³⁰ under the same conditions with a careful fractionation of the cracked products. *n*-Decane was obtained from the products of cracking paraffin wax, and other hydrocarbons were synthesized from corresponding bromides and iodides by the Wurtz reaction. The hydrocarbons were cracked at 425°C., 1 hour; 425°C., 3 hours; and 450°C., 1 hour. The final pressure was about 40 atm. The conditions of cracking correspond very closely to the average values of the temperature-time factor of commercial cracking operations.

The principal results of this investigation are given in Table 5. The formation of hydrogen was very small, not exceeding 0.001 per cent by weight for the one-hour process and 0.04 per cent for the three-hour process at 425°C. An exception was the cracking of dotriacontane yielding 0.1 per cent of hydrogen.

All the fractions boiling below the boiling range of the paraffin cracked are specified as the decomposition products, and *vice versa* all the fractions above this boiling range are specified as the condensation products. The predominant decomposition fractions are marked in the table. The content of olefins in the middle fractions, boiling from 50 to 250°C., is from 30 to 40 per cent of the total. In addition to the olefins, the cracked fractions contain paraffins and naphthenes.

The data of Table 5 lead to the following general conclusions.

1. The cracking stability of high molecular paraffins decreases rapidly with increasing molecular weight. *n*-Decane, for instance, yields 27.5 per cent of cracking products, *n*-hexadecane 52.1 per cent and dotriacon-

Table 5. Cracking of High Molecular Weight Paraffins.

Hydrocarbon, Conditions of Cracking	Per Cent by Decomposition	Weight of Condensation	Products of Total Cracking	Predominant Fractions of Decomposition Products
<i>n</i> -Decane 425°C., 1 h.	18.2	9.3	27.5	Gases, pentane-pentene
<i>n</i> -Dodecane 425°C., 1 h.	18.3	11.7	30.0	Gases, pentane-pentene, heptane-heptene, octane-octene
Same 425°C., 3 h.	40.1	20.4	60.5	Same fractions
Same 450°C., 1 h.	58.9	17.5	76.4	Same fractions
<i>n</i> -Hexadecane 425°C., 1 h.	40.9	11.2	52.1	Gases, pentane-pentene, octane-octene, nonane-nonene, 180–200°C.
Same 425°C., 3 h.	85.3	14.7	100.0	Gases, pentane-pentene, octane-octene, 180–200°C.
Dotriacontane 425°C., 1 h.	76.9	7.6	84.5	Gases, octane-octene, nonane-nonene, C ₁₆ fraction
Diisoamyl ¹¹³ 425°C., 1 h.	29.4	6.8	36.2	
Isohexadecane 425°C., 1 h.	53.3	10.2	63.5	Gases, pentane-pentene, octane-octene, nonane-nonene

tane 84.5 per cent under the same conditions of cracking, *i.e.*, 425°C. and 1 hour.

2. The cracking stability of iso-paraffins is slightly lower than that of normal hydrocarbons of the same molecular weight. *n*-Decane, for instance, yields 27.5 per cent of cracked products versus 36.2 per cent for diisoamyl at 425°C. and 1 hour.

3. Dehydrogenation of high molecular weight paraffins does not occur to any appreciable extent. Very small amounts of hydrogen formed can be due partially to some secondary reactions.

4. The break-down of paraffin molecules occurs at every carbon-carbon bond with some predominance at the middle of molecules. As a result, *n*-decane and *n*-dodecane produce a large amount of C₅ and C₆ fractions, *n*-hexadecane produces predominantly C₈ and C₉ fractions, together with C₅ fraction as a product of the secondary cracking of C₉ fraction primarily formed, etc.

5. The decomposition reactions predominate over the condensation reactions in the cracking of paraffins, particularly for less stable high molecular weight paraffins and iso-paraffins. As will be shown later, the cracking of olefins gives quite different results, forming largely the condensation products. It is very likely that the condensation products formed in the cracking of paraffins are due to the secondary condensation reactions of the olefins formed in the first stage of cracking.

The cracking of commercial paraffin wax is of particular interest because of the availability of this product. The cracked fractions may be produced in large quantities and may be carefully studied. Some results of the cracking of commercial paraffin wax of melting point 57–58°C. by

Sachanen and Tilicheyev¹¹³ are summarized in Table 6. This paraffin wax is composed mostly of $C_{24}H_{50}$, $C_{25}H_{52}$ and $C_{26}H_{54}$.

Table 6. Cracking Paraffin Wax.

			Yields of Cracked Products by Weight						Gaseous Olefins
Conditions of Cracking Temp. (°C.)	Press. (Atm.)	Time (Min.)	Gasoline to 410°F.	Kerosene 400°-590°F.	Residuum Above 590°F.	Carbon	Hydrogen	Gaseous Paraffins	
425	10	63	13.1	11.8	70.4	0.00	0.0005	2.8	1.1
425	10	183	42.4	18.4	26.6	0.00	0.028	6.2	2.4
450	15	125	59.2	17.3	8.7	0.05	0.14	7.6	2.3
450	25	184	60.0	11.6	4.7	2.95	0.35	18.1	5.0

The data on the distillation and chemical composition of the liquid cracked products (gasoline and kerosene) obtained in the cracking at

Table 7. Properties of 50°C. Cuts from Cracked Paraffin Wax.

Cuts (°C.)	% by Wt.	Sp. Gr. at 15°C.	Aniline Point (°C.)	Iodine No.	% Olefins in Cut	% Paraffins in Cut	Sp. Gr. of Paraffins	Mol. Wt.
30-50	4.2	0.642
50-100	11.0	0.689	41.2	153.2	45.3	54.7	0.672	80
100-150	20.2	0.735	45.3	120.8	50.1	49.8	0.716	112
150-200	18.6	0.755	56.7	101.2	52.2	47.8	0.744	140
200-250	29.6	0.780	68.7	71.9	52.1	47.9	0.765	184
250-300	16.4	0.791	79.6	50.5	43.3	56.7	0.782	220

425°C. are given in Table 7. The amount of olefins in the fractions was calculated on the basis of iodine numbers and molecular weights of the fractions. The paraffins were obtained after the removal of olefins by treatment with sulphuric acid and redistillation. As will be seen later, the cracked fractions of paraffin wax consist predominantly of olefins and paraffins, and the removal of olefins gives more or less pure paraffins.

The data of Table 6 clearly show that the formation of hydrogen is practically absent in the first stage of cracking, accompanied by formation of 13 per cent of gasoline. A small formation of hydrogen in the further steps of cracking should be attributed to some secondary reactions. In other words, the dehydrogenation reaction is almost entirely absent in the cracking of high molecular weight paraffins, as has been also stated by Tilicheyev and Feigin.

The products of cracking consist predominantly of paraffins and olefins. The low values of specific gravity of the fractions (Table 7) correspond to the mixtures of paraffins and olefins. The specific gravities of the fractions treated with sulphuric acid and redistilled (paraffins of Table 7) correspond to paraffins containing a small proportion of naphthenes. Paraffins and olefins are distributed in fractions almost in equal amounts as should be expected, taking into consideration the splitting of a paraffin molecule into two molecules of paraffin and olefin of a lower molecular weight.

Paraffins and olefins of various molecular weights and boiling ranges are formed, but the fractions boiling between 200-250°C. are to a certain extent predominant. These fractions contain paraffins and olefins con-

sisting of 12, 13 and 14 carbon atoms, or approximately one-half of the carbon atoms of the virgin paraffin. Thus, the breakdown of the carbon-carbon bonds in the cracking of high molecular weight paraffins takes place at every carbon-carbon bond but more frequently in the middle parts of the molecule, as has been also found by Tilicheyev and Feigin.

The production of paraffins and olefins of a lower molecular weight in almost pure state in the first stage of cracking of paraffin waxes may be used for the preparation of pure olefins and paraffins. Almost pure paraffins may be obtained by the treatment of cracked paraffin wax distillates with sulphuric acid and subsequent redistillation. On the other hand, more or less pure olefins may be obtained by the treatment of the same distillates with certain solvents under adequate conditions.

The rate of cracking of high molecular paraffins is closely expressed by the equation for monomolecular reactions. A possibility of bimolecular splitting reactions for these hydrocarbons seems to be highly improbable.

From the thermodynamic standpoint, low pressures are favorable to the reactions of cracking of paraffins, including dehydrogenation and splitting reactions. In practice, however, the adverse effect of moderately high pressures up to 100 atmospheres on the decomposition of paraffins may be almost negligible for two reasons. First, only very high pressures of the magnitude of 200-300 atmospheres may be sufficient to prevent the decomposition of a paraffin and perform the reverse reaction of alkylation, as will be discussed later. Secondly, the olefins formed as a result of the aforementioned reactions take practically no part in the equilibrium with the virgin paraffins because of many secondary reactions, such as for instance polymerization, cyclization, etc. The reactions of cracking are practically irreversible.

The decomposition of paraffins follows approximately the law of monomolecular reactions (compare Chapter 2). The velocity constants, k , of the decomposition of low molecular weight paraffins are given as follows:

	at 425°C.	at 575°C.
Methane	1.3×10^{-13}	3.3×10^{-9} ^{73a}
Ethane		8×10^{-5} at 565°C.
Propane		1.5×10^{-3} ³⁶
<i>n</i> -Butane	1.9×10^{-6}	4.8×10^{-3} ³⁶
iso-Butane		4.8×10^{-3} ³⁶
<i>n</i> -Pentane	2.4×10^{-6}	5.7×10^{-3} ³⁶
iso-Pentane	3.7×10^{-6}	6.5×10^{-3} ³⁶
<i>n</i> -Hexane	1.1×10^{-5}	15×10^{-3} ³⁶
iso-Hexane		21×10^{-3} ³⁶

The velocity constants of the decomposition of high molecular weight paraffins C_{12} to C_{32} at 425°C. under 150 atm. pressure are expressed by the following equation:

$$k = (2.3n - 15.6) \times 10^{-5},$$

where n is the number of C atoms (Tilicheyev^{129b}).

The decrease in the kinetic stability of paraffins with increasing molecular weight is clearly seen from the above data.

Burk and Laskowsky^{14a} summarized the data of the activation energy of the paraffin decomposition for C₄-C₈ paraffins and found that the average value for these hydrocarbons is in the range 63,000 \pm 500 cal. In the publication cited Tilicheyev gives the average value of the activation energy for normal C₅-C₁₀ paraffins as 65,000 cal. and for C₁₁-C₃₂ paraffins as 60,000 cal. Steacie and Puddington^{124b} summarize the activation energies of the decomposition of paraffins in the following table:

Methane	79,000 cal.	iso-Butane	63,500 cal.
Ethane	70,000 "	n-Pentane	56,000 "
Propane	62,000 "	iso-Pentane	55,000 "
n-Butane	59,000 "		

Catalytic Cracking of Paraffins

The action of such catalysts as certain heavy metals or alumina on the decomposition reactions of paraffins has been discussed in the previous paragraphs. The action of other catalysts can give quite different results. The following classification of the catalysts may be useful as a simplified scheme of the catalytic phenomena in cracking paraffins.

1. The catalysts which greatly weaken the carbon-carbon and hydrogen-carbon bonds and cause a complete decomposition of paraffins into carbon and hydrogen or carbon, hydrogen and methane (ethane). The catalysts of this type are such heavy metals as platinum, nickel, copper and some others.

2. The catalysts which greatly weaken the carbon-carbon bonds and particularly hydrogen-carbon bonds and produce a series of decomposition and condensation products. Aluminum chloride is a very active catalyst of this type, catalyzing the cracking at low temperatures. Ferric chloride, zinc chloride and some other chlorides belong to this type, but are less active than aluminum chloride.

3. The catalysts which weaken the carbon-hydrogen bonds and produce the dehydrogenation of paraffins to olefins and hydrogen. Carbon, alumina and chromic oxide belong to this type of catalyst, described in one of the previous paragraphs.

4. The catalysts which weaken the carbon-carbon bonds and perform splitting reactions, forming olefins and paraffins of a lower number of carbon atoms. To this type of catalyst belong the oxides and sulphides of molybdenum, vanadium, tungsten and some other heavy metals. The action of these catalysts is less selective, and they may catalyze the dehydrogenation reactions also.

5. The catalysts which slightly weaken both carbon-carbon and hydrogen-carbon bonds and mildly accelerate all cracking reactions. Activated clays, and some other adsorptive materials represent the catalysts of this type.

The present paragraph is confined only to the catalysts of types 2, 4

and 5. It should be kept in mind that, with the exception of aluminum chloride, the activity of the catalysts breaking the carbon-carbon and hydrogen-carbon bonds is not particularly great. As a result, these catalysts may be employed only at comparatively high temperatures close to those of non-catalytic cracking. It explains why the catalytic action of these substances has been recognized only during the last years.

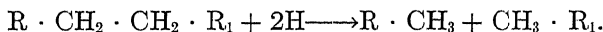
The catalytic or pseudo-catalytic action of aluminum chloride on the splitting reactions of paraffins, as well as of other hydrocarbons, has been well known for a number of years. Paraffin hydrocarbons are easily decomposed in the presence of aluminum chloride at such low temperatures as 200°C. and lower. The presence of water or hydrogen chloride promotes the reaction. In the absence of these substances the reaction is slow or takes place at higher temperatures.

Two layers are formed as a result of the reaction between paraffins and aluminum chloride. The upper layer consists of saturated hydrocarbons, and the lower layer, or the so-called aluminum chloride-hydrocarbon complex, contains aluminum chloride and unsaturated hydrocarbons belonging to polymers, cyclic olefins, highly unsaturated hydrocarbons and tars.

Calingaert and Beatty¹⁵ investigated the cracking of normal heptane with aluminum chloride under mild temperature conditions; 100 parts of normal heptane reacted produced:

pentanes and below	64.6
hexanes	5.8
heptanes (isomers)	5.2
polymerized products (lower layer)	24.4

The absence of appreciable amounts of high-boiling paraffins, as well as of naphthenes and aromatics, in the upper layer should be mentioned. Under more severe temperature conditions, high molecular weight paraffins and naphthenes are formed, in addition to low molecular weight paraffins. According to Nenitzescu,⁹⁰ the primary action is the activation of hydrogen by aluminum chloride. As a result, the dehydrogenation reactions proceed, forming hydrogen and olefins. The hydrogen *in statu nascendi* attacks paraffins and produces paraffins of lower molecular weight, *e.g.*,



The olefin formed reacts further in the presence of the same catalyst producing cyclic hydrocarbons by isomerization and polymers by polymerization. The olefins and polymers are further decomposed into highly unsaturated products forming tar and coke. As a result, the liquid non-viscous products of the decomposition of paraffins in the presence of aluminum chloride are entirely saturated, consisting predominantly of paraffins and naphthenes. Thus, the cracking of paraffins in the presence of aluminum chloride is complicated by many side reactions and consecutive reactions, promoted by the same catalyst. The isomeriz-

ing action of aluminum chloride on paraffins will be discussed later. The cracking catalytic activity of phosphoric acid is much lower than that of aluminum chloride. Petrov and Cheltsova^{107a} cracked hexadecane non-catalytically and catalytically at 440-460°C. under pressure of 20-76 atm. for 1 hour. Phosphoric acid was used as a catalyst in the amount of 20 per cent by weight. The non-catalytic cracking yielded 67 per cent of liquid products of which 27 per cent boiled below 200°C. The catalytic cracking gave 57 per cent of liquid products of which 35 per cent boiled at 200°C. or over.

Some other metallic halides, such as ferric chloride, zinc chloride, zirconium chloride, etc., catalyze the splitting reactions of paraffins at higher temperatures than does aluminum chloride.

Very little experimental material has been published on the catalytic action of metallic oxides in cracking hydrocarbons. Oxides of molybdenum, vanadium and some other heavy metals may appreciably accelerate the rate of decomposition of paraffins at high temperatures. As will be shown in Chapter 3, the rate of gasoline formation increases considerably in destructive hydrogenation in the presence of such hydrogenation catalysts as molybdenum compounds. Thus, these compounds may catalyze two different reactions—hydrogenation and decomposition.

Some experiments on the catalytic action of many inorganic compounds on the cracking of petroleum products will be discussed in Chapter 2.

Many porous adsorbents accelerate the rate of cracking, including splitting and dehydrogenation reactions. Egloff, Morrell, Thomas and Bloch²⁶ investigated the catalytic cracking of normal octane and cetane in the presence of activated clay. The experiments with normal octane could be compared with those of Marschner⁸² who investigated the non-catalytic cracking of normal octane at the same temperature (570°C.). The rate of the catalytic decomposition of this hydrocarbon increases 7-8 times in comparison with the non-catalytic process. The difference in the composition of cracking products is not less significant. Table 8 gives the comparative results of the catalytic and non-catalytic cracking of normal octane.

Thus, the non-catalytic cracking results in greater yields of methane, ethane and ethene, as well as in smaller yields of C_3 - C_5 hydrocarbons, as compared to the catalytic process. The catalyst directs the decomposition to the middle parts of molecules. On the other hand, a comparatively strong formation of hydrogen shows that dehydrogenation reactions are also accelerated by the catalyst.

The induced decomposition of paraffins as well as other hydrocarbons should be briefly mentioned in conjunction with catalysis. Hydrocarbons can be decomposed in the presence of such compounds as metallic alkyls, ethene oxide, etc., to a much greater degree than when they are decomposed alone under the same temperature conditions.^{17a} For instance, normal heptane and decane are decomposed at 200-265°C. in the

Table 8. Chemical Composition of Cracked Products in Catalytic and Non-Catalytic Cracking of Normal Octane at 570°C.

Run	Catalytic	Non-Catalytic
Temperature (°C.)	570	570
Contact Time (Seconds)	1	12.7
Decomposition (%)	11.0	19.4
Mols of Products per Mol of Octane Cracked	2.4	3.24
Complete Product Analysis, Mols per 100 Mols of Octane Cracked		
H ₂	13	0.3
CH ₄	9	77
C ₂ H ₄	19	86
C ₂ H ₆	11	55
C ₃ H ₆	52	46
C ₃ H ₈	18	6.5
C ₄ H ₈	22	18
C ₄ H ₁₀	7	1.3
C ₅	73	15
C ₅ , Weight % of Charge	16	21
Loss, Weight % of Charge	2.2	0.8

presence of tetraethyl lead. These phenomena are explained mostly from the standpoint of the theory that free radicals, liberated by the decomposition of added compounds, induce the decomposition of hydrocarbons. This theory appears to be a plausible, but not a necessarily correct, explanation of the mechanism of induced cracking. Induced reactions are very common in the oxidation of inorganic and organic compounds in solutions, in which the mechanism of the induced reactions does not involve the theory of free radicals. The inhibiting action of such compounds as nitrogen oxide on the decomposition of paraffins is also interpreted from the standpoint of the theory of free radicals and chain reactions.^{124b}

Alkylation of Paraffins

The production of paraffins by alkylation of low molecular weight paraffins with olefins is one of the most interesting and promising problems in the field of thermal and catalytic conversion of hydrocarbons. The alkylation of gaseous paraffins with gaseous olefins is particularly important from the commercial point of view. By this means cheap gaseous hydrocarbons may be converted into liquid hydrocarbons for aviation and motor gasolines. The synthetic gasolines, produced by alkylation and consisting predominantly of paraffins, are much more stable than the products of cracking or polymerization. On the other hand, by the alkylation of isoparaffins and isoölefins, highly branched isoparaffins may be synthesized, having octane numbers as high as 100-125.

An advantage of alkylation is the one-stage operation leading to the formation of hydrocarbons of high octane number. Another method of synthesizing these hydrocarbons is the selective polymerization of isoölefins followed by hydrogenation, as will be described later in this chapter. Thus, the last method is performed in two stages, the second one being the comparatively expensive process of hydrogenation. In

addition, alkylation almost doubles the yield of synthetic paraffins as compared with the polymerization-hydrogenation method, in which only olefins are utilized.

The alkylation of paraffins with olefins is a synthetic reaction, the reverse of the splitting decomposition. As a result of this reaction, a paraffin and an olefin form a paraffin of a higher molecular weight and a higher boiling point. Thermodynamic equations (7) and (8) with reverse signs may be applied to the alkylation of paraffins.

For instance, the free energy of alkylation of normal butane with ethene



may be expressed by the equation

$$\Delta F^\circ = -20,200 + 32.4T \quad \Delta F^\circ < 0 \text{ below } 350^\circ\text{C.} \quad (11)$$

According to equation (11), the free energy of alkylation, ΔF° , is strongly negative at low temperatures. Thus, the alkylation reactions are thermodynamically possible at low temperatures.

The experiments show that the alkylation of paraffins with olefins takes place at low temperatures in the presence of various catalysts, which overcome a well-known inactivity of hydrocarbons at low temperatures. The catalysts of alkylation are some strong acids, boron fluoride, aluminum chloride and chlorides of some other metals, such as iron, zirconium, etc. Iso-paraffins are much more reactive than normal hydrocarbons with respect to alkylation. In the presence of the aforementioned catalysts, the tertiary hydrogen of iso-paraffins is activated and becomes able to react with olefins or with esters formed from olefins, yielding alkylated paraffins. Normal paraffins do not react with olefins under these conditions. In some cases, however, as, for instance, in the presence of aluminum chloride, alkylation of normal paraffins becomes possible due probably to a preliminary isomerization of normal paraffins to iso-paraffins effected by the same versatile catalyst.

The investigations of Ipatieff⁶⁴ show that normal and isobutanes, isopentane and normal hexane can be alkylated with ethene in the presence of aluminum chloride. The temperature of the reaction is from room temperature to 60-70°C. The proportion of catalyst used is from 10 to 30 per cent by weight with reference to the paraffin. A small percentage of hydrogen chloride is added during the reaction for activation of aluminum chloride. The reaction products consist mostly of paraffins distilling in a rather wide boiling range. The alkylation of isobutane with ethene in the presence of zirconium chloride requires a higher temperature, 100°C. In the presence of boron fluoride, powdered nickel and water, iso-paraffins may be alkylated at room temperature.

Recently Birch, Dunstan, Fidler, Pim and Tait⁷ discovered that iso-paraffins are alkylated with olefins in the presence of an excess of concentrated sulphuric acid at the low temperatures of -10 to +30°C. The

pressure is low—atmospheric or somewhat higher—if the reaction takes place with volatile hydrocarbons at higher temperatures up to 30°C. Addition of the olefin to the mixture of paraffin and sulphuric acid is carried out over a period of 1-1½ hours, followed by a further 30 minutes of agitation. The yields of the synthetic hydrocarbons are fairly high, from 106 to 167 per cent with respect to the olefin used. The synthetic hydrocarbons boil in a comparatively wide range up to 260°C. The octane number of the synthetic hydrocarbons boiling in the range of gasoline is from 82 to 92 without leading. The consumption of sulphuric acid in a once-through operation is high, amounting to 100-200 per cent with reference to the synthetic product; but the deterioration of the spent acid per pass is comparatively small, and the spent acid may be reused. The final consumption of sulphuric acid amounts to 32 per cent by weight. It is lower in the continuous operation.

In a later communication the same authors^{7a} showed that the yields and octane numbers of synthetic gasolines depend upon the ratio of iso-paraffin to olefin in the reaction. Higher ratios give better yields and higher octane numbers. Moreover, fractionation of the synthetic gasolines shows that comparatively pure iso-paraffins of the expected structure are obtained with a high ratio of iso-paraffin to olefin. The data in Table 9 illustrate the yields and octane numbers at various ratios.

Table 9. Alkylation of Isobutane with Propene in the Presence of Sulphuric Acid.

Iso-paraffin to olefin ratio:	1:1	4:1
Synthetic gasoline, % on olefin taken	124	200
Specific gravity	0.698	0.692
Bromine number	1	1
Octane number	82.5	89.1
O. N. + 1 cc. T.E.L.		96.2
O. N. + 1½ cc. T.E.L.	93.3	

Isobutene and its polymers reacting with isobutane form practically the same alkylation products. On the other hand, both isobutene and the normal butenes also yield practically identical products. Thus depolymerization of polymers and isomerization of the olefins take place before alkylation.^{7b}

In addition to the alkylated paraffins of the expected molecular weight, the alkylated products contain paraffinic hydrocarbons of a lower and higher molecular weight or boiling range. The formation of these is an evident result of the secondary reactions. The main secondary reaction is probably the scission of iso-paraffins into a paraffin and an olefin in the presence of sulphuric acid. The realkylation of various paraffins and olefins formed with the virgin hydrocarbons may be responsible for the formation of iso-paraffins of various molecular weights.

The fouling of sulphuric acid is apparently due to the dehydrogenating effect of sulphuric acid on olefins, resulting in the formation of highly unsaturated hydrocarbons soluble in sulphuric acid. The unsaturates formed are separated on dilution of the fouled sulphuric acid with water.

These reactions investigated by Nametkin and his associates will be described later.

Thus the alkylation of paraffins with olefins in the presence of sulfuric acid is complicated, and is accompanied by many side and secondary reactions.

The mechanism of the catalytic alkylation of paraffins is apparently closely related to that of the polymerization of olefins. The formation of esters of sulfuric acid or of positive alkyl ions (Whitmore) from olefins are probable intermediate reactions, to be described later in this chapter. The activation of the iso-paraffins is a simultaneous process, the nature of which is unknown. In the final stage the formation of alkylated paraffins takes place as a result of the reaction between the activated paraffin and the ester or positive alkyl ion.

In commercial continuous operation¹ isobutane is alkylated with butenes. The process is carried out at low temperatures of 0 to 5°C. (32-41°F.) with a very efficient stirring, which is obtained by means of a pump recycling acid-hydrocarbon emulsion through a system of jets or baffles. According to the data given above, the feed to reactors contains an excess of isobutane, from 4 to 5 parts of isobutane to one part of butenes. 98-per cent acid is used for the reaction. The contact time is from 5 to 20-40 minutes. The spent acid is of 90 per cent strength. The consumption of acid is approximately 20 per cent by weight, or one pound per gallon of the synthetic product.

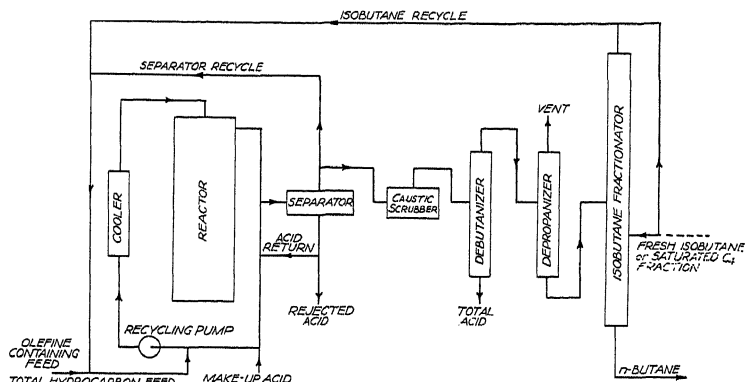
The ratio of isobutane to butenes consumed in the reaction is close to the theoretical molar or weight ratio 1:1. In practice, the consumption of isobutane is slightly greater than the theoretical. The ratio of isobutane to butenes in cracked gases does not usually exceed 1:3, so that the additional amount of isobutane required must be supplied from field gases. The ratio of acid to hydrocarbons in the reactor is about 1:1, but in some cases it may be as high as 2:1. As has been mentioned above, part of the butenes is dehydrogenated in the presence of sulfuric acid, forming highly unsaturated hydrocarbons soluble in acid, and decreasing the concentration of the acid.

The yield of alkylate averages 170-200 per cent by volume with respect to butenes used. The octane number of the alkylate is about 92-93 by the Motor method, 100 after leading with 0.5 cc. of tetraethyl lead and 100 + 0.4 cc. after leading with 3 cc. of tetraethyl lead. The high-boiling fractions of the alkylate boiling from 300 to 400°F., can be used as safety fuel. The yield of these fractions is about 15 per cent of the total alkylate. The properties: API gravity 57, octane number (clear) 81, and, after leading with 3 cc., 94 (*Nat. Petroleum News*, p. R-20, Jan. 24, 1940).

The alkylation of propene and isobutene gives approximately the same yields of alkylate but the consumption of sulfuric acid is higher, up to 2.6 pounds per gallon of alkylate, and the octane number is lower (88).

Cracked gasolines can also be alkylated with isobutane under the same conditions. As a result, the gasolines become entirely saturated and increase the octane number to 77. The consumption of acid, however, is great, up to 3.3 pounds per gallon of alkylated product.

The flow diagram of an alkylation plant is given in Figure 1. The synthetic product from the reactor is separated into alkylate and low-boiling fractions in a debutanizer. The latter are further separated from propane in a depropanizer. The butane fraction is finally fractionated in



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 1.—Sulphuric Acid Alkylation Plant.

a powerful fractionating column for the separation of isobutane and normal butane. Isobutane is recycled to the reactor. The ratios given above of isobutane to butenes, as well as of acid to hydrocarbons, are maintained in the reactor. The plant shown in Figure 1 has a single reactor. In commercial practice several reactors are arranged in parallel or in series.

The process of alkylation in the presence of sulfuric acid, developed mostly by the Anglo-Iranian Oil Company, is being offered for commercial use. Six units are reported to be in operation and eight units are under construction and consideration (November, 1939). The total production of alkylated paraffins in this country will reach approximately 11,000 barrels per day by the middle of 1940.

Blunck and Carmody⁸ described the alkylation of paraffins with olefins in the presence of double salts of aluminum chloride such as LiAlCl_4 , NaAlCl_4 . The temperature of the process was 154–281°C. (310–555°F.) and the pressure about 1000 pounds per square inch gauge. Isobutane was alkylated with ethene, propene and isobutene. The total yields of synthetic gasolines increased with increasing molecular weight of the olefin used, but the polymerization and formation of polyolefins interfere more in the case of isobutene than of ethene and propene.

The high-temperature alkylation of paraffins with olefins at tempera-

tures about 300°C. (572°F.) is thermodynamically impossible under atmospheric pressure, since the free energy, ΔF° , of this reaction is strongly positive at high temperatures under atmospheric pressure. The free energy of alkylation, however, depends on the pressure according to the equation:

$$\Delta F = -RT \log \text{nat } P + \Delta F^\circ, \quad (12)$$

where ΔF is the free energy under the pressure P . Thus, a higher pressure must be maintained to make the free energy of alkylation negative and the process thermodynamically possible. For instance, the positive value of ΔF° of reaction (11) at 600°C. and atmospheric pressure -48,080 cal. can be changed to zero cal. by increasing the pressure from one to about 100 atmospheres, and to negative values at higher pressures. In these approximate calculations pressures are assumed to be equal to fugacities.

Another drawback to the high-temperature alkylation of paraffins is the polymerization of olefins, which can easily interfere with the first process. As will be shown later, the polymerization of olefins has about the same values of free energy ΔF° and is thermodynamically as probable as the alkylation of paraffins (equations 11 and 14). The olefins, however, have a greater tendency to mutual combination than to alkylation of paraffins. The interference of polymerization in the alkylation of paraffins may be suppressed by using comparatively small concentrations of olefins, in the neighborhood of 10-15 per cent or lower.

Frey and Hepp³⁷ investigated the alkylation of propane and isobutane with ethene at 504-520°C. (940-968°F.) and under pressures up to 4,500 pounds per square inch gauge. The relative amount of ethene was very low, and the reaction took place with a large excess of a paraffin hydrocarbon. The duration of the process was 4-5 minutes. Under these conditions, alkylation is the predominant process: the greater part of the ethene was transformed into pentanes (with propane) or hexanes (with isobutane).

Keith and Ward⁷⁴ described experiments on cracking gaseous paraffins and olefins at 429-453°C. (800-850°F.) and 800 pounds per square inch pressure gauge. The yield of gasoline formed was roughly 30-60 per cent higher than the quantity of olefins converted into polymers. Direct determinations have shown that the amount of ethane, propane and butane decreases after the processing due to alkylation reactions, as the authors believe. However, the pressure used in these experiments should be considered to be too low for alkylation.

Nothing has been done on catalysts for the alkylation of paraffins at high temperatures. It is a well-known fact that a catalyst is equally active for a direct and a reverse reaction. From this standpoint, it should be expected that such catalysts as activated clays, compounds of molybdenum, etc., should accelerate the high-temperature alkylation of paraffins under the proper conditions of temperature and pressure.

Oberfell and Frey report^{94a} that the thermal alkylation of paraffins with olefins is performed by the Phillips Petroleum Company on a semi-commercial scale. Isobutane and propane are alkylated with ethene and propene at temperatures of 505 to 510°C. (943 to 950°F.) under pressures of 4,500 to 6,300 pounds. The temperature 486°C. (907°F.) and a pressure of 8,000 pounds were used for alkylation of isobutane with isobutene, evidently in view of a lower thermal stability of octanes formed. The reaction time is from 2.2 to 7.4 minutes. The olefin is added during reaction at a predetermined rate to keep the concentration of olefin low and to avoid polymerization. In contrast to catalytic alkylation, the decreasing order of the activity of olefins is: ethene, propene, *n*-butenes, isobutene. As to the paraffins, normal paraffins and isoparaffins are alkylated thermally with equal ease. Ethane and methane react with difficulty. The yield of synthetic products per pass under the above conditions is from 11 to 35 per cent by weight.

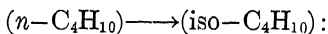
The alkylation of isobutane with ethene is of particular interest, producing neohexane or 2,2-dimethylbutane. Neohexane has a high octane number (around 95) and a higher volatility as compared with isoöctane (b.p. 50°C). The leaded blend of isoöctane and neohexane may produce aviation fuels of very high octane number (up to 115) and of desired ASTM distillation. In the semi-commercial operation ethene is obtained by cracking gases containing ethane at temperatures of 760-815°C. (1400-1500°F.) and low pressures of about 20-50 pounds.

The diagram of the Phillips thermal alkylation plant is given in Figure 1a. The diagram is self-explanatory. It should be mentioned that the low concentration of olefin is attained by pumping the ethene-isobutane mixture to a manifold which distributes it among 10 inlets situated along a reaction tube coil, as is shown in the figure.

Isomerization of Paraffins

A possibility of the isomerization of paraffins is closely related to the stability of various isomers. As has been stated above, the stability of isoparaffins is regarded as somewhat lower than that of normal paraffins (equation 2). In some cases, however, isoparaffins may be more stable than normal hydrocarbons. Schultze and Weller¹²⁰ have found that the thermal stability of isobutane is higher than that of normal butane. In any case the difference in the stability of various isomers of a paraffin is not great, and, from the thermodynamic standpoint, an equilibrium between the various isomers would exist at a given temperature. According to Parks and Huffman⁹⁹ and equation 2, this equilibrium would be displaced to the side of the normal paraffin with increasing temperature.

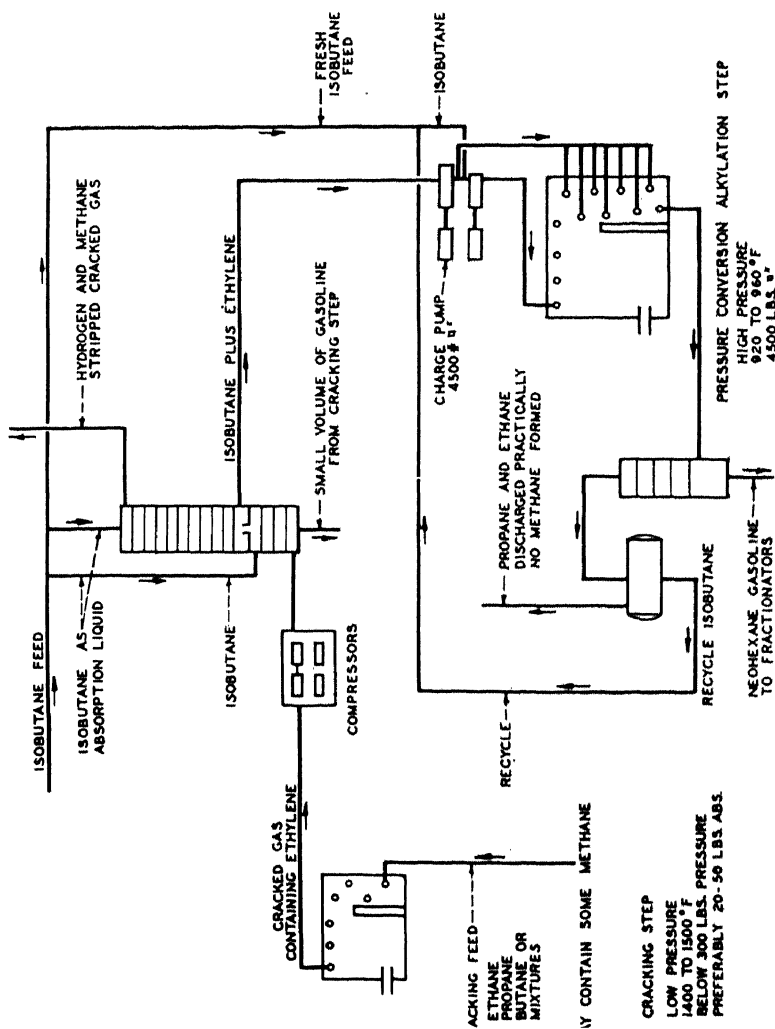
Parks, Schomate, Kennedy and Crawford¹⁰¹ have calculated the ΔF° equation for the isomerization of butane:



$$\Delta F^\circ = -1,630 + 5.8T$$

FIGURE 1a.—Thermal Alkylation (Neohexane) Plant.

Courtesy "Refiner and Natural Gasoline Manufacturer"



According to this equation, an equilibrium mixture of the butanes at 527°C. (980°F.) should contain 87 per cent of the normal and 13 per cent of the isobutane.

The isomerization of paraffins at lower temperatures may have some practical aspects, particularly for such hydrocarbons as normal butane, pentane, hexane and highly paraffinic naphthas of very low octane number. A partial isomerization of normal paraffins would appreciably increase the octane number of these hydrocarbons and products.

The isomerization of *n*-butane into isobutane is of particular interest in view of the expansion of low-temperature alkylation of isobutane described above. The content of isobutane in cracked gases is entirely insufficient for the alkylation of the butenes present. Thus an additional amount of isobutane must be supplied from an outside source, as for example from field gases.

The isomerization of paraffins, however, does not occur in the thermal process. Schulte and Weller¹²⁰ cracked normal butane and isobutane at 700°C. for 0.32 second, producing 20 per cent of decomposition products. Neither isobutane nor isobutene, in the cracking of normal butane, and neither normal butane nor normal butene, in the cracking of isobutane, could be detected in the decomposition products.

In the presence of certain catalysts the conditions for isomerization are much more favorable. The catalytic isomerization of paraffins may take place at low temperatures, even at room temperature.

Moldavsky, Kobilskaya and Lifschitz⁸⁷ treated normal hexane and octane with aluminum chloride in the presence of hydrogen chloride at a temperature of 20-90°C., the time of reaction being 1-24 hours. They found that up to 25 per cent of isoparaffins were formed as a result of the treatment.

According to Calingaert and Beatty,¹⁵ normal heptane refluxed with aluminum chloride formed about 6 per cent of isoheptanes. Nenitzescu and Dragan⁹² refluxed normal hexane or heptane in the presence of aluminum chloride and found isohexanes or isoheptanes in addition to many decomposition products.

Petrow, Meschtscheriakow and Andreiew¹⁰⁸ isomerized normal heptane and octane in the presence of various catalysts and hydrogen or nitrogen at temperatures of 200 to 440°C. The amount of the isoparaffins formed was determined by the method of Schaarschmidt (see Chapter 5). The results for normal heptane are given in Table 10.

Table 10. Isomerization of Normal Heptane.

Catalyst	Temp. (°C.)	Time, (Hours)	Isomerization (%)
Zinc chloride, 5%	300	6	27
Same, 5%	400	7	18
Aluminum chloride, 1%	220	3	8
Molybdenum sulphide, 5% and copper oxide, 5%	400	7	15

Ipatieff and Grosse⁶⁵ treated normal butane with aluminum chloride,

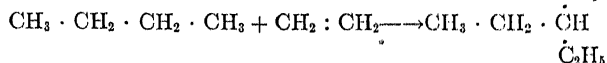
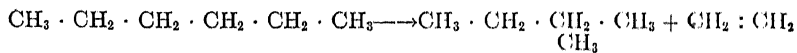
in the presence of hydrogen chloride at elevated temperatures. As a result, about 13 per cent of isobutane was formed in addition to the decomposition products.

The most amazing results were obtained by Glazebrook, Phillips and Lovell⁴⁴ for the isomerization of normal pentane. In the presence of aluminum bromide (about 10 per cent by weight), as much as 55.9 per cent of isopentane was produced from normal pentane at room temperature. The proportion of decomposition products was very small.

Yuriev and Pavlov¹⁵⁰ isomerized normal octane into isoöctanes at 300-310°C. in a stream of hydrogen. The catalysts used were platinum on activated carbon, nickel on alumina, nickel on zinc oxide, alumina and activated carbon. The relative proportion of the catalysts was about 20 per cent with respect to the carriers. The isomerization in the presence of platinum on carbon was about 15 per cent, in the presence of nickel on zinc oxide about 10 per cent, the other catalysts being less active.

Montgomery, McAteer and Franke⁸⁸ studied the isomerization of normal and isobutane at room temperature in the presence of aluminum bromide. The equilibrium was attained from both sides after 1000-1400 hours and corresponded to about 75-80 per cent isobutane. Traces of hydrogen bromide increase the rate of the process considerably. The experiments with normal pentane in the presence of the same catalyst showed even a higher conversion to isopentane than that found by Glazebrook, Phillips and Lovell. The latest data published by Moldavsky and Nisovkina^{87a} show that the isomerization of butanes with aluminum chloride is a reversible process leading to equilibrium between normal and isobutane. The percentage of isobutane in the equilibrium mixtures decreases with increasing temperature from 79 at 70°C. to 58 at 180°C.

The mechanism of isomerization of paraffins is not quite clear. According to Ipatieff and Grosse,⁶⁵ it is a secondary process following the splitting decomposition of paraffins into low molecular weight paraffins and olefins induced by the catalyst. Some of the paraffins and olefins formed are recombined in the process of alkylation, producing the paraffins of iso-structure. For instance:



According to Nenitzescu,⁹⁰ the temperature conditions of the process, as well as the formation of certain isomers, are in disagreement with the mechanism of Ipatieff and Grosse. The temperature of catalytic isomerization is lower than that of decomposition in the presence of aluminum chloride. On the other hand, the isomerization of normal butane into isobutane cannot be explained by the mechanism suggested by Ipatieff and Grosse. The isomerization of paraffins in the presence of aluminum

chloride may be a primary process owing to the activation of hydrogen atoms.

Montgomery, McAteer and Franke⁸⁸ recognize that catalytic isomerization of paraffins at low temperatures is due to the hypothetical dissociation of the hydrocarbon-catalyst complex into two ions, and the rearrangement of the cation by H or CH₃ shifts. The recombination of the rearranged cation and original anion would produce the isomer. The catalytic isomerization of normal butane and pentane to corresponding isoparaffins in the presence of aluminum chloride and hydrogen chloride at moderate temperatures of about 150-200°C. can be performed on a commercial scale, yielding up to 60 per cent isomers [U.O.P. Fr. P. 823,-595 (1938); N. V. de Bataaf Petroleum Matsch. Fr. P. 843,204 (1939)].

Aromatic Cyclization of Paraffins

Aromatic cyclization of paraffins at moderate temperatures is undoubtedly caused by certain intermediate reactions involving olefins formed as primary decomposition products, but the exact mechanism of this reaction remains obscure. The possible intermediate reactions will be discussed in the paragraphs confined to olefins. The high yields of aromatics in catalytic aromatization are obtained from the paraffins whose structure allows direct formation of a benzene ring. Other paraffins do not produce aromatics in large amounts.

The Russian authors contributed much to the cyclization of paraffins. Moldavsky and Kamusher⁸⁵ transformed normal hexane, heptane, octane and diisomyl at temperatures of 460-470°C. and in the presence of chromic oxide or molybdenum sulphide into aromatic hydrocarbons. The yields of aromatic hydrocarbons were about 20 per cent. The structure of the aromatics formed corresponds to that of paraffins, for instance, normal hexane gives benzene; normal heptane yields toluene; normal octane gives ethylbenzene and *o*-xylene, etc. According to Moldavsky, Kamusher and Kobilskaya,⁸⁶ the aromatic products formed contain olefins also. The same authors and Moldavsky, Besprosvannaya, Kamusher and Kobilskaya⁸⁴ investigated other catalysts of cyclization, *i.e.*, zinc oxide, titanite oxide, molybdenum oxide, molybdenum sulphide, and active charcoals at higher temperatures up to 550°C. Titanite oxide, and molybdenum oxide and sulphide are the most active catalysts for this reaction.

Kasansky and Plate⁷³ transformed normal octane, diisobutyl and diisomyl into aromatic products at 300-310°C. with platinum-carbon catalyst. Normal octane, for example, produces ethylbenzene and *o*-xylene. The yield of aromatic hydrocarbons is from 10 to 25 per cent. The formation of isoparaffins is also observed.

Karzev, Severianova and Siova⁷² studied the aromatization of normal decane at 500-550°C. in the presence of chromium oxide-copper oxide-phosphoric acid catalyst and found 45 per cent aromatic hydrocarbons in the liquid products of the process.

Grosse, Morrell and Mattox⁴⁹ obtained similar results on the catalytic

aromatization of paraffins. They transformed straight-chain paraffins into aromatics at 450-700°C. and atmospheric pressure. Oxides of chromium, molybdenum, vanadium, titanium, etc., supported on activated alumina, were employed as catalysts. The contact time was less than 100 seconds. Normal hexane was cyclized into benzene, normal heptane into toluene and normal octane into ethylbenzene and xylenes, in accordance with the results of Moldavsky and his co-workers.

Taylor and Turkevich¹²⁹ produced pure aromatic hydrocarbons from normal hexane at slow rates of flow of heptane at 468°C. with chromium oxide gel as catalyst.

Summary of Cracking Reactions of Paraffins

On the basis of the foregoing paragraphs, the most probable cracking reactions of paraffins are: splitting decomposition, forming a paraffin and an olefin, and dehydrogenation, forming the olefin of the same carbon number. The probability of dehydrogenation decreases with increasing molecular weight of the paraffin. The high molecular weight paraffins for the most part undergo various carbon-carbon splitting decomposition reactions, the rupture of the chain taking place at various carbon-carbon bonds, but most frequently in the middle of the chain.

The partial alkylation of paraffins with olefins at high temperatures may take place under sufficiently high pressures. The isomerization of paraffins is improbable in the non-catalytic process.

These processes are the primary decomposition reactions of the paraffins. A series of secondary reactions follows the primary reactions, and these involve the formation of low molecular weight paraffins and olefins. The former are mostly decomposed further or partially alkylated, if the pressure is high. The olefins are either polymerized or further decomposed, depending on the conditions of cracking. On the other hand, they may be transformed into naphthenes or aromatics. All these reactions will be discussed in the next paragraphs.

UNSATURATED HYDROCARBONS

Unsaturated hydrocarbons are usually absent in straight-run products. They are formed in the first stages of cracking and are involved in further reactions. Olefins are the principal unsaturated hydrocarbons in cracked products.

The range of olefins formed in cracking is not as large as that of virgin paraffins, varying from ethene to olefins with about 15 carbon atoms in a molecule. Gaseous olefins from ethene to butenes and liquid olefins from pentenes to pentadecenes predominate. The content of high molecular weight olefins is not significant. The high-boiling cracked fractions consist mostly of various cyclic hydrocarbons. Cyclic olefins and diolefins are formed in comparatively small amounts. The presence of such unsaturated hydrocarbons as the derivatives of acetylene or terpenes is doubtful.

The following discussion is confined mostly to the olefins, as they are the most important unsaturated hydrocarbons formed in cracking processes.

Free Energy of Olefins

According to Thomas *et al.*,¹³⁴ the free energy of normal olefins (above ethene) may be approximately expressed by the following equation:

$$\Delta F^\circ = 20,321 - 5,835n - 33.26T + 24.52nT \quad (13)$$

The equation relates to the normal olefins having a double bond in the terminal position (1-olefins). According to Parks and Huffman,⁹⁹ the free energy of an olefin decreases, *i.e.*, the stability increases, as the double bond becomes more centrally placed within the molecule.

The branching of the chain has probably the same effect as in the case of paraffins. Thus the decreasing order of stability of the butenes is: normal 2-butene, normal 1-butene and isobutene. The rate of decomposition of the butenes and other olefins corresponds approximately to this scheme. According to Goldwasser and Taylor,^{45a} however, *n*-hexene and *n*-heptene are less stable than the isomers at 400°C. in the presence of alumina and thoria.¹⁵²

Equation (13) shows that the free energy of formation of any olefin at cracking temperatures is positive as in the case of paraffins; or, in other words, that the olefins are thermodynamically unstable with respect to the elements. As can be calculated, the olefins are equally unstable with respect to decomposition into methane (ethane) and elements.

As in the case of paraffins, however, all these reactions do not occur at cracking temperatures less than 600-700°C. (1112-1292°F.) and in the absence of certain active metallic catalysts. In their presence the rate of such reactions increases enormously, and the reactions take place at comparatively moderate temperatures. Sabatier and Senderens¹¹¹ and Cantelo¹⁸ decomposed ethene and propene into hydrogen, carbon and methane (ethane) in the presence of nickel at 300-350°C. Hurd and Meinert⁵⁹ showed that the decomposition of propene into free elements or methane and elements in Monel tubes takes place at 350°C. and is complete in 30 seconds. Hurd⁵⁶ decomposed 25 per cent isobutene in Monel tubes at 410°C. in 17 seconds. It is also known that ethene at high temperatures and under high pressure decomposes rapidly and sometimes with an explosion, with formation of carbon, methane and hydrogen.

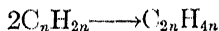
This type of complete decomposition of olefins may be of importance at temperatures above 700°C. At the temperatures of commercial cracking and in the absence of the above-mentioned metallic catalysts, other reactions of olefins, including polymerization, depolymerization, formation of diolefins, etc., are much more important and of greater extent.

Polymerization of Olefins

Polymerization and depolymerization of olefins are reversible reactions at least under certain conditions of temperature and pressure.

Aliphatic monoolefins are as likely to polymerize as are cyclic monoolefins. Aliphatic and cyclic diolefins, particularly with conjugated double bonds, are much more polymerizable than monoolefins. The polymerization of aliphatic monoolefins is of primary importance from the commercial standpoint. The aliphatic monoolefins are the sole unsaturates present in cracked gases and predominate in cracked gasolines.

The free energy of the polymerization of normal olefins (above ethene)



may be expressed by the following equation:

$$\Delta F^\circ = -20,320 + 33.26T \quad \Delta F^\circ < 0 \text{ above } 333^\circ\text{C}. \quad (14)$$

Normal and isoolefins are formed as a result of polymerization, but the equation has been calculated for normal olefins only because of the insufficiency of the free energy values for isoolefins.

The free energy of polymerization of ethene to normal butene differs from equation (14) and is expressed as follows:

$$\Delta F^\circ = -24,400 + 32.0T \quad \Delta F^\circ < 0 \text{ above } 491^\circ\text{C}. \quad (15)$$

Thus, the value of ΔF° for the polymerization of ethene is more negative than for high molecular weight olefins, other conditions (temperature and pressure) being equal. In other words, thermodynamically ethene is more suitable for thermal polymerization than are olefins of a higher molecular weight. As will be seen later, however, the rate of polymerization of ethene is lowest in the catalytic process.

It should be mentioned that polymerization may take place between two different molecules of olefins, as for instance:



Equation (14) shows that the loss of free energy and the polymerization tendency of olefins decrease with an increase in temperature. High temperatures above 500°C . (932°F .) are more favorable to depolymerization, if the pressure is low. On the contrary, high pressures favor polymerization (equation 12). For instance, zero value of free energy of polymerization corresponds to 333°C . at atmospheric pressure. By increasing the pressure to about 100 atmospheres ΔF° can be changed from zero to -5600 cal. The value of ΔF° of the same reaction at 550°C . ($+7100$ cal.) can be changed to -450 cal. by increasing the pressure to 100 atmospheres. Thus, a pressure of about 100 atmospheres is sufficient for partial polymerization of olefins at 550°C . (1022°F .).

For the polymerization of gaseous isobutene to gaseous diisobutene Parks and Todd¹⁰⁰ give the following equation:

$$\Delta F^\circ = -17,920 + 42.2T \quad \Delta F^\circ < 0 \text{ above } 152^\circ\text{C}. \quad (16)$$

Thus, the decrease in the free energy of polymerization of isoolefins is less than that of normal olefins at the same temperature. The poly-

merization of isoölefins at high temperatures above 500°C. (932°F.) requires a higher pressure than in the case of normal olefins. On the other hand, the isoölefins are kinetically more reactive, and the rate of polymerization may be much higher for them than for normal olefins, particularly in the catalytic process. This high reactivity of isoölefins may be used for selective catalytic polymerization of isoölefins under conditions of temperature and pressure at which normal olefins are not polymerized.

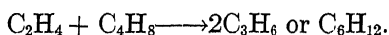
Although the free energy of polymerization is greatest at low temperatures, rather high temperatures or powerful catalysts must be used to overcome the passivity of olefins and to increase the rate of polymerization.

In the thermal process at high temperatures, suitable high pressures must be employed in order to make ΔF negative, as has been explained above.

The following selective data on the thermal polymerization of olefins in the absence of catalysts illustrate the foregoing conclusions.

Hague and Wheeler⁵¹ found that ethene at 400-450°C. and atmospheric pressure yields only butenes as polymers. The time of the reaction was 3 hours and the conversion was only 3.5-8 per cent of the ethene. According to Pease,¹⁰³ the polymerization of ethene predominates at 450-475°C. and atmospheric pressure.

Storch^{124c} investigated more thoroughly the thermal polymerization of ethene at 377°C. and 141.5 mm. pressure, the time of the reaction being 1-3 hours. A series of olefins was formed, including mostly propene, butene and hexenes. Butene is considered as a primary product of polymerization, producing other olefins as a result of secondary polymerization with ethene, as for instance:



Pease¹⁰⁴ studied the polymerization of ethene under higher pressures at 350-500°C., the time of reaction being from $\frac{1}{4}$ hour to 8 hours. Under these conditions, at least 50 per cent of the ethene was polymerized without the formation of more than 1-2 per cent of hydrogen and methane. Some of his results are given in Table 11.

Table 11. High Temperature Polymerization of Ethene.

Temperature (°C.)	Initial Pressure of Ethene (Atm.)	Time (Hours)	% by Volume of Ethene Reacted
350	9.85	8.0	30.7
375	9.80	4.0	37.0
400	9.05	2.0	47.9
425	10.03	0.25	17.8
450	9.73	0.25	42.3
475	4.96	0.25	45.8
500	2.56	0.25	41.3

Ethene is much more suitable for thermal polymerization than other olefins. The polymerization of pure ethene at 450°C. and 50 atm. pres-

sure is accompanied by strong evolution of heat, in some cases causing violent explosions. It should be mentioned, however, that a small proportion of ethene is present in cracked gases (Chapter 7) so that thermal polymerization of cracked gases is quite a safe operation.

The polymerization of other olefins gives results similar to those obtained in the polymerization of ethene. This process is very slow at temperatures of 350 to 400°C. and at moderate pressures up to 10 atmospheres: it requires many hours to convert 20-40 per cent olefins under these conditions (Table 11). On the other hand, at higher temperatures of about 500°C. or more and atmospheric pressure, depolymerization and other decomposition processes are probable, particularly for higher molecular weight olefins, as will be shown later. Thus, a sufficiently high, but not excessive temperature of about 500-550°C. (932-1022°F.) and a correspondingly high pressure of about 100 atmospheres must be used for the thermal polymerization of olefins, particularly diluted with paraffins, as usually occurs in commercial practice.

The polymerization of olefins is a typical bimolecular reaction. The extra surface does not influence the reaction, indicating that the polymerization is homogeneous.^{110a} The activation energy of polymerization is about 38,000-42,000 cal. and is approximately the same for all low molecular weight olefins from ethene to hexene.^{89a} The low value of the activation energy of polymerization, particularly compared with that of decomposition of paraffins (60,000-65,000 cal.), explains the predominance of polymerization reactions in moderate-temperature treatment of hydrocarbon gases containing paraffins and olefins.

The thermal polymerization of olefins may be induced by oxygen, lead alkyls, azomethane, etc. As in the case of paraffins, these phenomena are believed to involve the theory of free radicals.

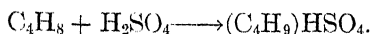
Diolefins have a much greater tendency to polymerize than monoolefins. Of the monoolefins, only styrene is as polymerizable as diolefins. Butadiene and isoprene (as well as styrene) are polymerized at low temperatures of about 50°C. and at high pressures of 5000 to 7000 pounds, while aliphatic olefins remain unchanged under these conditions (Starkweather^{124a}). The catalytic polymerization of diolefins and styrene proceeds very easily at low temperatures and pressures.

As will be shown later in this chapter, diolefins and cyclic olefins are formed at high temperatures and in the advanced stages of cracking. Under these conditions, polymerization of these unsaturates seems to be improbable, particularly taking into consideration the low concentration of the diolefins and cyclic olefins formed.

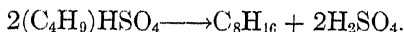
Catalytic Polymerization of Olefins

As has been stated in the previous discussion, thermodynamically polymerization of olefins is a low-temperature process. Many catalysts can be used to bring about polymerization of olefins at low temperatures up to 300°C. (572°F.).

With sulphuric acid the olefins may be polymerized at room temperature or slightly elevated temperatures up to 100°C. The reaction of sulphuric acid with olefins takes place in two phases, the first of which is thought to be the formation of an ester, as for instance:



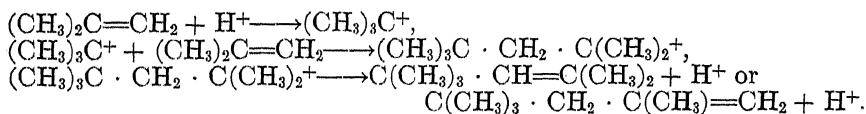
As a result of this reaction, the olefin is dissolved in sulphuric acid. The second phase of the process may be either the formation of an alcohol by hydrolysis of the ester or polymerization by the reaction:



Thus, sulphuric acid is regenerated and can be used further. The second phase of the process depends upon the properties of the olefin, concentration of sulphuric acid, and temperature conditions of the reaction. With increasing molecular weight of olefins, polymerization becomes the predominant reaction.¹² Under the same conditions, C_7H_{14} yields 72 per cent alcohol and 12 per cent polymers, and $\text{C}_{12}\text{H}_{24}$ yields 97 per cent polymers and only a trace of alcohol. A high concentration of sulphuric acid, as well as a high temperature, favors the formation of polymers. Isoölefins are more reactive toward sulphuric acid than normal olefins of the same molecular weight. The commercial application of polymerization of low molecular weight olefins in the presence of sulphuric acid will be discussed later.

Ipatieff and his associates⁶⁴ developed a catalytic process of polymerizing olefins, using phosphoric acid as a catalyst. In the presence of phosphoric acid propene and butenes are readily polymerized at temperatures of 204 to 232°C. (400 to 450°F.) and under moderate pressures of about 100-200 pounds per square inch gauge. The polymerization of ethene under these conditions is only partial and does not exceed 30 per cent. Ethene requires a higher temperature, *i.e.*, about 296-324°C. (565-615°F.) and a higher pressure, *i.e.*, 520 pounds.

According to Whitmore,^{140a} the polymerization of olefins in the presence of sulphuric acid and similar catalysts is brought about by the intermediate reactions of hydrogen ion with olefins. A hydrogen ion is combined with a molecule of olefin, forming a positive alkyl ion. In the same way the positive ion adds to the second molecule of olefin. The positive composite ion formed decomposes, liberating a hydrogen ion and forming a dimer. The following equations may be applied to isobutene:



According to Ipatieff,⁶⁴ the mechanism of polymerization of olefins by phosphoric acid is the same as in the case of sulphuric acid. As the first stage of the reaction, an ester of phosphoric acid is formed, which is

decomposed in the second stage, yielding the dimer and regenerating the phosphoric acid. The intermediate ester may be isolated under mild temperature conditions. One mol of phosphoric acid is capable of producing 100 mols or more of polymers before the activity of the catalyst is lost due to the formation and deposition of carbonaceous materials.

It is of interest that the hydrocarbons present in polymerized gasolines are mostly C_7 and C_8 hydrocarbons. This fact proves that the polymerization as well as the interpolymerization of propene and butenes takes place mainly between two molecules.

If the temperature of the process is mild, polymerization with phosphoric acid yields mostly polymerized olefins as primary products. For instance, propene polymerized at 135-200°C. and 1-15 atmospheres pressure, or butene polymerized at 30-130°C., produce almost pure olefins of various molecular weights. It is of interest to notice that the polymers of isobutene polymerized at 30°C. contained only two polymers, *i.e.*, diiso- and triiso-butene. Under more severe conditions, various other hydrocarbons were formed.⁶³

Monroe and Gilliland^{87b} studied the catalytic polymerization of propene in the presence of dilute phosphoric acid. The polymerization is stepwise. The first step is the formation of the dimer, which in turn reacts with more propene forming the trimer, and the latter then forms the tetramer.

The data and rules for predicting the structures of olefinic polymers are discussed in the articles of Hoog and his associates^{54a} and of Wachter.¹³⁷

The olefinic polymers formed in polymerization are considered as primary products of the process. They may be partially transformed into naphthenes as a result of the cyclization of olefins. On the other hand, the naphthenes also may be the primary decomposition products of the above-mentioned intermediate esters. Actually the polymerized gasolines contain not only olefins and naphthenes, but also paraffins and aromatics, the latter particularly in high-boiling fractions. According to Ipatieff, the formation of aromatics is due to the dehydrogenation of naphthenes under the conditions of the catalytic process. The hydrogen liberated in this reaction transforms a part of the olefins into paraffins.

Dunstan and Howes²⁰ also investigated the polymerizing action of phosphoric acid and of some of its salts.

According to Brandes, Gruse and Lowy,⁹ zinc chloride polymerizes propene at temperatures of 150 to 310°C. under high pressures of about 1500 pounds per square inch gauge and higher. The yield of liquid products is as high as 74 per cent.

Ingold and Wasserman^{60a} showed that black sulphur compounds of heavy metals mildly catalyze the polymerization of olefins at moderate temperatures (150-250°C). Konaka^{76a} polymerized ethene in the presence of cobalt and nickel catalysts at temperatures of 250 to 290°C. and under atmospheric pressure.

In the presence of floridin a slow polymerization of propene takes place at 350°C. and atmospheric pressure,⁴³ whereas isoölefins are readily polymerized at room temperature and at still lower temperatures.

Aluminum chloride readily polymerizes low molecular and high molecular weight olefins. Polymerization is only the first stage of the process, and is followed by secondary reactions forming naphthenes, paraffins and aromatics. The formation of high-boiling fractions is much more pronounced than in the case of the acid catalysts. In the presence of small amounts of the catalyst and under proper temperature conditions, lubricating oils may be produced as a result of the polymerization of gaseous and liquid olefins with aluminum chloride as a catalyst. The cyclization processes accompany the polymerization of olefins with aluminum chloride even at such low temperatures as -35° or -78°C.^{188a} However, high molecular weight hexadecene polymerized at room temperature in the presence of aluminum chloride or boron trifluoride produces only "true" polymers without cyclization.

Hall and Nash^{51a} showed that the cracking action of aluminum chloride on oils is almost completely inhibited by the presence of metallic aluminum or magnesium. The catalyst aluminum chloride-metallic aluminum is a predominantly polymerizing catalyst producing highly olefinic polymerization products.

The last investigations of Nametkin, Abakumovskaya and Rudenko^{88a} contributed much to the clarification of secondary reactions of olefins in the presence of such catalysts as sulphuric acid, aluminum chloride, etc. The polymerization of olefins is the first stage of reactions induced by the catalysts. In the second stage, some of the polymers formed are dehydrogenated in the presence of these catalysts, producing highly unsaturated hydrocarbons easily convertible into resinous substances. The hydrogen liberated saturates other polymers and transforms them into paraffins. The above reactions in the presence of aluminum chloride are complicated by the cracking action of this catalyst resulting in the formation of low-boiling hydrocarbons.

The results of Nametkin *et al.* are in accord with the peculiar ability of aluminum chloride and similar catalysts to activate certain hydrogen atoms of hydrocarbons. This activation is responsible for the hydrogenation and dehydrogenation reactions, described above, as well as for the alkylation of iso-paraffins discussed in a previous section. It should also be mentioned that minute amounts of oxygen accelerate the polymerization of olefins.^{124a} In contrast to the above catalytic heterogeneous polymerization, the action of oxygen is an example of homogeneous catalysis.

Polymerization and Depolymerization of High Molecular Weight Olefins

The olefins formed as primary products of cracking of paraffins or paraffinic side chains can be polymerized or depolymerized, depending on the temperature-pressure conditions of the process. In processes using

high temperatures above 500°C. and low pressures (below 5 atmospheres), the depolymerization reactions of high molecular weight olefins may be predominant. In processes involving moderate temperatures of about 500°C. and high pressures (above 50 atmospheres), the conditions are favorable for polymerization reactions, although depolymerization reactions, particularly of high molecular weight olefins, may also occur. In catalytic polymerization processes at comparatively low temperatures of about 300°C. polymerization reactions become predominant, as has been demonstrated in the previous section. Moor and Schiliaiewa^{87c} studied the decomposition of diisobutene at temperatures of 492 to 641°C. under atmospheric pressure. Depolymerization to isobutene is the predominant reaction under these conditions. The yield of isobutene in the cracked products reaches 70 per cent at a conversion of about 15 per cent.

The relative occurrence of depolymerization and polymerization reactions in cracking high molecular weight olefins was studied by Tilicheyev and Feigin.¹³⁰ As olefins, *n*-decene (capriline) and hexadecene (cetene) were used. The physical constants of the decene used are: specific gravity at 15°/4°C., 0.729, boiling range 122-130°C.; and those of the hexadecene are: specific gravity at 15°/4°C., 0.790 and boiling range 120-140°C. at 3 mm. pressure.

The temperature of the experiments performed in bombs was 425°C. at a pressure of about 50 atmospheres; the time was 14 minutes and 1 hour. After the cracking was completed, the synthetic crude was separated into fractions as in the case of paraffin hydrocarbons. The fractions boiling below and above the boiling range of the virgin olefin were specified as decomposition and condensation products. The summarized results are given in Table 12.

Table 12. Cracking of High Molecular Weight Olefins.

Hydrocarbon, Conditions of Cracking	Per Cent by Decom- position	Weight of Conden- sation	Products of Total Cracking	Predominant Fractions
<i>n</i> -Decene, 425°C., 14 min.	5.0	23.5	28.5	Di- and tri-decene
Same, 425°C., 1 hour	21.2	38.8	60.0	Pentane-pentene, hexane-hexene, di- and tri-decene.
Hexadecene, 425°C., 14 min.	15.6	36.9	52.5	Dihexadecene.
Same, 425°C., 1 hour	43.1	27.2	70.3	Gases, hexane-hexene, octane-octene, nonane-nonene, 180-200°C.

The liquid products of cracking (decomposition and condensation) of *n*-decene at 425°C., 14 minutes, contained from 75 to 95 per cent of pure olefins, while in the further stages of the process the cracking products contained no more than 50 per cent olefins. The condensation products of *n*-decene are polymers, mostly di- and tri-decenes. The decomposition and condensation products of decene and hexadecene at 425°C. and 1 hour contain, in addition to olefins, paraffins, naphthenes and a small amount of aromatics. Thus, only in the first stages of cracking

olefins are depolymerization, and particularly polymerization, reactions predominant. As a result, olefins yield the olefins of lower and higher molecular weight by depolymerization and polymerization. In more advanced stages of the process other decomposition reactions of olefins and polymers take place readily.

The following general conclusions may be drawn as a result of this investigation:

1. In the first stage of cracking olefins, polymerization is predominant, while in the further steps the part of the decomposition reactions becomes more and more important.

2. The cracking stability of olefins decreases with increasing molecular weight, as in the case of paraffins. Other conditions being equal, the total conversion of *n*-decene is 28.5 per cent, and of hexadecene 52.5, per cent.

These data and the data on the cracking of paraffins of the same number of carbon atoms give an answer to the comparative thermal stability of paraffins and olefins under the same cracking conditions. The comparative data for normal decane and octene and for hexadecane and hexadecene are summarized in Table 13. The stability of normal decane and normal octane should be of about the same value, taking into consideration the almost equal stability of normal decane and dodecane (Table 5).

Table 13. Comparison of Decomposition and Condensation Reactions in Cracking Paraffins and Olefins at 425°C., 1 Hour.

Hydrocarbon	Per Cent by Weight of Products of		Total
	Decomposition	Condensation	
<i>n</i> -Decane	18.2	9.3	27.5
<i>n</i> -Octene	21.2	38.8	60.0
Hexadecane	40.9	11.2	52.1
Hexadecene	43.1	27.2	70.3

The data of Table 13 show that the extent of the decomposition reactions is about the same for paraffins and olefins of the same number of carbon atoms. On the contrary, the condensation reactions are predominant for olefins due to polymerization. Thus, the total effect of cracking is much greater for olefins than for paraffins.

These conclusions are valid for the moderate temperature conditions of commercial cracking under pressure. As has been stated above, the reactions of decomposition and depolymerization of olefins predominate at high temperatures and low pressures, while polymerization does not take place at all or is of secondary importance. Under these conditions, the thermal stability of olefins may be of the same order, or even somewhat greater, than that of paraffins. It should be kept in mind that the free energy of the formation of paraffins ΔF° , at high temperatures above 700°C. (1292°F.), becomes greater than that of olefins of the same C-atom number (equations 1 and 13).

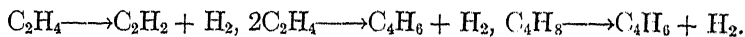
Egloff, Morrell, Thomas and Bloch²⁶ investigated the catalytic cracking of the olefins, normal octene and hexadecene, in the presence of

activated clay. They thoroughly studied the decomposition products but did not determine the amount and character of the condensation products formed in the cracking. As in the case of paraffins, the cracking rate of olefins is much greater in the catalytic process than in thermal cracking. The isomerization of olefins in catalytic cracking will be discussed later.

Other Decomposition Reactions of Olefins

Depolymerization of olefins is the simplest type of their decomposition. Two other types may be classified as dehydrogenation, and splitting into a paraffin and a diolefin. Both reactions take place in the advanced stages of cracking, particularly at high temperatures.

The dehydrogenation of olefins may be exemplified by the following reactions:



The free energy of the first reaction of the formation of acetylene from ethene is represented by the equation:

$$\Delta F^\circ = 45,000 - 32.0T \quad \Delta F^\circ < 0 \text{ above } 1133^\circ\text{C}. \quad (16a)$$

Thus, the dehydrogenation of ethene to acetylene and hydrogen is thermodynamically possible at very high temperatures (about $1000^\circ\text{C}.$). This reaction cannot take place to any appreciable extent at the temperatures of commercial cracking. Some experimental data on the formation of acetylene at moderate temperatures lower than $700^\circ\text{C}.$ may be due to analytical errors. According to Schultz,¹¹⁹ the formation of acetylene from ethene does not exceed 1.5 per cent at $777^\circ\text{C}.$

The free energy of decomposition of olefins leading to the formation of diolefins, as for instance butadiene, C_4H_6 , cannot be calculated at the present time due to the lack of free energy data for diolefins. Thomas, Egloff and Morrell¹³⁴ computed the free energy of formation of 1,3-butadiene partially from thermal and partially from spectroscopic data: ΔF° is 35,250 cal. for $298^\circ\text{K}.$ and 60,000 cal. for $1000^\circ\text{K}.$ On the basis of this computation, the free energy of formation of 1,3-butadiene may be expressed by the following equation:

$$\Delta F^\circ = 24,800 + 35.2T \quad (17)$$

Then the free energy of the dehydrogenation of 1-butene into 1,3-butadiene is as follows:

$$\Delta F^\circ = 28,900 - 32T \quad \Delta F^\circ < 0 \text{ above } 632^\circ\text{C}. \quad (18)$$

According to the last equation, butadiene is more stable than butene at temperatures above $632^\circ\text{C}.$ ($1211^\circ\text{F}.$). The formation of butadiene from butene in small amounts may be expected at lower temperatures of about 500 - $600^\circ\text{C}.$ (932 - $1112^\circ\text{F}.$). Wheeler and Wood¹⁴⁰ give the data on the formation of butadiene presented in Table 14.

Table 14. Formation of Butadiene in Cracking of Olefins.

Temperature (°C.)	—Per Cent by Volume of Butadiene—		
	Ethene	Formed From Propene	Butene
600	0.9
650	0.3	0.2	1.7
700	0.4	0.6	1.4
750	0.2	0.4	0.2
800	0.15	0.3	..

The formation of butadiene has a maximum corresponding to temperatures of 650 to 700°C. As might be expected, butene yields the maximum amounts of butadiene.

The temperature range of the formation of butadiene corresponds to the thermodynamic computations given above. The decrease in the percentage of butadiene with increasing temperature above 700°C. can be explained by the secondary reactions of this unstable hydrocarbon.

Frolich and Schneider⁴⁰ studied the decomposition of ethene at 725°C. and 0.2 atmosphere. They found that formation of butadiene and hydrogen is the predominant reaction under these conditions. As much as from 11 to 30 mols of butadiene per 100 mols of ethene reacting were formed. The authors suggest that the formation of butadiene is due to a reaction between two molecules of ethene, as has been represented by one of the foregoing equations.

Fedorov, Smirnova and Semenov³¹ found that a high yield of butadiene, 21 per cent, was obtained from 2-butene at 700°C., as a result of dehydrogenation.

M. Schultze and G. R. Schultze¹¹⁹ pyrolyzed ethene at temperatures of 777-848°C. for 1.517 to 0.208 sec. The yield of butadiene amounted to 30 per cent of the ethene reacted at 777-848°C. At higher temperatures butadiene is partially decomposed to acetylene and ethene



the reaction being reversible.

Grosse and his collaborators^{49c} have shown that catalytic dehydrogenation of olefins produces diolefins of the same carbon framework. Dehydrogenation was carried out at a temperature of 600 to 650°C. and at reduced pressure of about 0.25 atm. or lower. The catalysts used were chromium, molybdenum or vanadium oxides on alumina as a carrier. The single pass yields of diolefins varied from 20 to 30 per cent. Under these conditions 1,3-butadiene was formed from normal butenes, isoprene from the branched chain pentenes, and piperylene from 2-pentene.

A strong decomposition of diolefins with formation of acetylene, olefins and paraffins was observed by Hurd and Meinert at temperatures of 500-550°C.⁵⁹

The dehydrogenation reactions of olefins, as well as depolymerization, lead to the formation of olefins, diolefins and hydrogen. No paraffins are formed as a result of these reactions. In other reactions of the decompo-

sition of olefins, however, paraffin hydrocarbons are readily obtained, particularly those of low molecular weight, including methane and ethane.

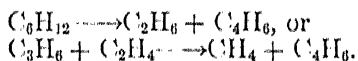
Investigations of the advanced stages of thermal decomposition of olefins at high temperatures are too numerous to be included in this book. Table 15, containing the results obtained by Wheeler and Wood¹⁴⁰ for the thermal decomposition of propene, gives a clear idea of the products of advanced decomposition of olefins. Very similar data were obtained by the same authors for ethene and butene.

Table 15. Decomposition of Propene at High Temperatures, Total Time of Heating from 20 to 10 Seconds.

—Yields in % by Weight—			Gas Analysis							
Temp. (°C.)	Liquid Products	Gasoline up to 170°C.	Coke	C ₃ H ₆ Unreacted	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	H ₂
650	5.2	3.2	Nil	86.9	4.1	0.2	2.5	7.7	2.1	0.5
700	20.3	12.9	Trace	45.6	6.5	0.6	7.9	23.5	18.9	7.05
750	35.6	20.4	"	10.4	2.0	0.4	6.8	37.0	49.1	14.4
800	40.6	19.0	1.7	1.5	0.5	0.3	5.4	28.1	70.7	23.6
850	33.8	14.6	9.5		0.5		4.5	18.6	85.9	36.7
900	11.9	6.8	Not Determined		0.5		3.1	8.0	86.1	66.5

At the temperatures of 800-900°C. (10 seconds) complete decomposition of propene to carbon, hydrogen and methane may be largely responsible for the formation of methane and hydrogen. It should be pointed out that this stage of the decomposition is accompanied by considerable formation of coke.

The formation of methane and ethane, however, starts in the less advanced stages of cracking, at temperatures of 700-750°C. Under these conditions the formation of coke is practically absent, and the above reactions of the complete decomposition do not occur to any appreciable extent. In this phase of the decomposition of olefins, other reactions yielding paraffins and diolefins without coke formation may take place, as for instance:



The calculation of the free energy for the first of these reactions gives the following equation:

$$\Delta F^\circ = 18,000 - 31.3T \quad \Delta F^\circ < 0 \text{ above } 302^\circ\text{C}. \quad (19)$$

The reactions of this type are thermodynamically probable at very moderate cracking temperatures. However, their rate should be very small at moderate temperatures. As is well known, the diolefins are not formed at moderate cracking temperatures. It is probable that the reactions in question readily occur at high temperatures above 500°C. (932°F.). Reactions of this type may be largely responsible for the formation of paraffins from olefins. The diolefins formed undergo secondary condensation reactions leading to the formation of aromatics, as will be shown later in this chapter.

Pease and Morton¹⁰⁶ investigated the decomposition of pentene-2 at 550°C. In addition to the depolymerization and formation of butene, they postulated the reaction forming butadiene according to the equation:



Hurd and his associates^{56a} showed that the formation of methane from isobutene is one of the primary decomposition reactions of isobutene at 650-700°C. under atmospheric pressure.

Thus, the thermal cracking of olefins is complicated by many side reactions. The first phase of cracking is polymerization, particularly under high pressures, accompanied by depolymerization. In more advanced stages, at higher temperatures and/or greater process times, olefins are dehydrogenated and decomposed with formation of diolefins, paraffins and hydrogen. In the most advanced steps at high temperatures the decomposition of olefins into carbon, methane and hydrogen takes place readily. This scheme does not include the cyclization and aromatization processes, which are discussed later.

Hydrogenation of Olefins

The free energy of hydrogenation of olefins to corresponding paraffins, ΔF° , is expressed by the following equation:

$$\Delta F^\circ = -30,870 - 55n + 31.06T + 0.68nT \quad (20)$$

This equation shows that the values of ΔF° , *e.g.*, for an olefin with 10 carbon atoms, are negative at low and moderate temperatures not exceeding 556°C. (1033°F.). Thus, from the thermodynamic standpoint, the hydrogenation of olefins is a low and moderate temperature process. At higher temperatures a reverse process of dehydrogenation of paraffins occurs, as has been discussed above. It is evident that high pressures are favorable to hydrogenation.

The hydrogenation of olefins at low and moderate temperatures, however, cannot be actually performed in the absence of catalysts. Only at high temperatures (about 500-600°C.) can the low molecular weight olefins, such as ethene, propene and butenes, be partially hydrogenated, as has been stated above. Pease and Durgan¹⁰⁵ hydrogenated ethene at 600-700°C.; and Frey and Smith³⁹ hydrogenated ethene and propene at 575°C., the pressure being one atmosphere or a little less. Under high pressures of hydrogen up to 100-200 atmospheres, hydrogenation of olefins takes place non-catalytically at temperatures lower than 500°C. However, Waterman and van Vlodrop^{139a} have found that *n*-octene does not undergo hydrogenation with high pressure hydrogen (110-120 kg/cm² initial hydrogen pressure) without a catalyst at temperatures of 250 to 360°C. The reaction seems to be very sensitive to the presence of catalysts in minute amounts and can be carried out "non-catalytically" in old autoclaves, due probably to a thin layer of catalyst on the walls.

In a new autoclave *n*-octene subjected to non-catalytic hydrogenation under the aforementioned conditions was practically unaltered.

On the contrary, catalytic hydrogenation of olefins can be easily carried out at very moderate and even low temperatures. The most active catalysts for this process are platinum, palladium, nickel, cobalt, iron and copper. In the presence of these catalysts the hydrogenation of olefins proceeds rapidly at room and lower temperatures. For instance, Hansford and Emmett⁵² hydrogenated ethene in the presence of iron catalyst at -90°C . Higher temperatures up to $200\text{--}300^{\circ}\text{C}$. favor the rate of catalytic hydrogenation. It should be remembered, however, that at 300°C . and higher temperatures, hydrogenation is accompanied by the decomposition of olefins into elements, which is catalyzed by the same metals.

It is well known that the above-mentioned metallic catalysts are very sensitive to the presence of various poisons, particularly sulphur compounds, which are usually present in petroleum products. The olefins to be hydrogenated in the presence of such catalysts must be practically sulphur-free. The catalysts resistant to the poisonous action of sulphur compounds, such as the oxygen and sulphur compounds of molybdenum, chromium, etc., hydrogenate olefins at moderate temperatures and elevated pressures. These catalysts are largely used in the commercial hydrogenation of oil products and will be discussed in Chapter 3.

Polymerization of gaseous olefins and hydrogenation of the polymers formed may be carried out simultaneously in the presence of polymerizing and hydrogenating catalysts such as, for instance, phosphoric acid and molybdenum catalyst. The reaction temperature is about 300°C . and the pressure about 100 atm. Under these conditions polymerization of olefins and hydrogenation of the polymers formed are claimed to be two predominant reactions, while the rate of hydrogenation of initial olefins may be insignificant [U.O.P. Br. P. 492, 728 (1938)].

The hydrogenation of olefins does not play any important part in cracking due to the low concentration of hydrogen in the products of cracking and the absence of catalysts. This process is of primary importance in hydrogenating oil products in which process the reactions are performed catalytically and under high hydrogen pressure.

Isomerization of Olefins

The values of free energy of formation of various isomers of an olefin are very close and, theoretically, isomerization of olefins is as feasible as that of paraffins. Practically it is of more importance for olefins due to the greater reactivity of these hydrocarbons. On the other hand, olefins can form more isomers than paraffins. In addition to the isomerization of chains, isomerization due to the shift of double bonds, as well as isomerization into cyclic hydrocarbons may be possible. The last type will be studied in the next paragraph.

Frey and Huppke³⁸ dehydrogenated normal butane in the presence

of chromic oxide gel at a temperature of 350-500°C. They found that all isomers of butenes—1-butene, *cis*-2-butene and *trans*-2-butene—were formed under these conditions in the ratio 25:30:45, corresponding to the equilibrium between the isomers.

Hurd and Goldsby⁵⁷ investigated the isomerization of butenes at 500-700°C., the time of reaction being from 8 to 12 seconds. Under these rather severe conditions, the decomposition of 1- or 2-butene is accompanied by isomerization. The unreacted, recovered 1-butene is partially isomerized into 2-butene and, *vice versa*, 2-butene produces some 1-butene. 2-Butene is the most stable isomer.

Ipatieff, Pines and Schaad⁶⁸ catalytically isomerized 1-butene into 2-butene at moderate temperatures. At 249°C. and 7.8 atmospheres pressure in the presence of diatomaceous earth impregnated with phosphoric acid, isomerization was found to be complete, contrary to the results of Frey and Huppke.

A partial isomerization of 1-pentene into 2-pentene and *vice versa* at temperatures of 580-600°C., in 13-19 seconds, was shown by Hurd, Good-year and Goldsby.⁵⁸ It is of interest that the conditions of isomerization were very close to those found by Hurd and Goldsby for butenes.

In an earlier experiment, Ipatieff⁶¹ isomerized isopropylethene in trimethylethene at temperatures of 450-535°C. in the presence of alumina.

According to Norris and Reuter,⁹⁴ isopropylethene is isomerized into trimethylethene at 425°C., in 16 seconds, to the extent of 47 per cent in the presence of aluminum sulphate, and at 500°C., in 14 seconds, to the extent of 29 per cent in the presence of phosphoric acid.

Laughlin, Nash and Whitmore⁷⁷ showed that tetramethylethene, methylisopropylethene and *t*-butylethene passed over phosphorus pentoxide on silica gel at 300°C. gave the same mixture of these isomers in the ratio 61:31:3. This very interesting experiment, as well as that of Frey and Huppke, proves that an equilibrium between various isomers of a hydrocarbon can really exist, in accordance with small variations of free energy for various isomers.

Petrow, Meschtscheriakow and Andreiew¹⁰⁸ partially isomerized 1-hexene into 2-hexene at 400°C., 1 hour, in the presence of 5 per cent of molybdenum sulphide. The isomerization of normal hexene into dimethylethylethene at 325-350°C. and pressure of 60 atm. in the presence of phosphoric acid was observed by Petrov and Scoukine.^{107b}

Very interesting data on the isomerization of various olefins were obtained by Egloff, Morrell, Thomas and Bloch.²⁶ The experiments were performed in the presence of activated clay. Normal butenes were partially isomerized into isobutene at temperatures of 385-600°C. In addition to isomerization, various products of cracking were formed. The ratio of isobutene to normal butene was as high as 0.3-0.4 for the fraction of C₄ hydrocarbons. Pentene-1 was processed at 400°C. The C₅-

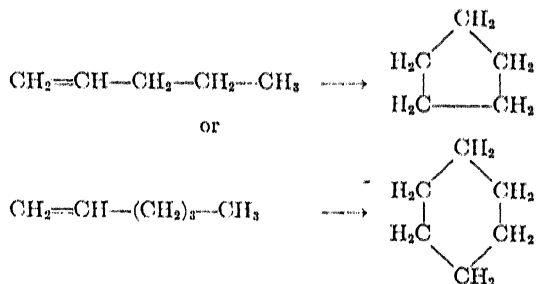
fraction consisted of 82 per cent of isopentene. Normal octene was cracked at temperatures of 375-400°C. Under these conditions, the polymerization was very pronounced. For instance, after cracking at 385°C. approximately 80 per cent of the C_8 -fraction consisted of isoöctenes. Methylheptene, dimethylhexenes and trimethylpentene were detected among the isomers. Cetene, when cracked at temperatures of 300-450°C., is found to be isomerized to a large extent, forming isoöctenes. The olefins produced by cracking cetene were largely isoölefins. According to the authors, the isomerization of high molecular weight olefins precedes decomposition in cracking with activated clay.

The above investigations show that isomerization of olefins occurs more easily and more frequently than that of paraffins. The isomerization of olefins in the presence of various catalysts may be a very common phenomenon in catalytic cracking. In the thermal process isomerization takes place at high temperatures, largely accompanied by other cracking reactions. Taking into consideration the great instability of olefins at high temperatures which is involved in various polymerization reactions, decomposition, etc., it is not believed that the isomerization of olefins would play an important part in thermal cracking. On the other hand, in the catalytic processes the isomerization of olefins may proceed to a large extent and may be used for the production of gasolines rich in the branched aliphatic hydrocarbons.

Cyclization and Aromatization of Olefins

In the advanced stages the cracking of olefins yields various naphthenes and aromatic hydrocarbons. For instance, the liquid products of the high-temperature cracking of propene (Table 15) contain a large proportion of aromatic hydrocarbons. Under the same conditions, paraffins also form highly aromatic gasolines and other products. It is very probable, however, that in cracking paraffins the formation of olefins precedes aromatization, and that aromatics and naphthenes are formed from olefins which are primary decomposition products of paraffins. It should be kept in mind that the direct or quasi-direct cyclization of paraffins into aromatics takes place only in the presence of specific catalysts.

The formation of naphthenes from olefins may be due to the cyclic isomerization of olefins, as for instance:



The isomerization of normal 1-hexene into cyclohexane has a free energy as follows:

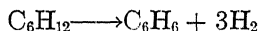
$$\Delta F^\circ = -19,200 + 23.6T \quad \Delta F^\circ < 0 \text{ below } 540^\circ\text{C.} \quad (21)$$

Thus, the cyclic isomerization of hexene gives negative values of free energy up to 540°C. and very small positive values at higher temperatures up to 700°C. The reaction is thermodynamically possible at the temperatures of commercial cracking. However, there is no direct evidence of isomeric cyclization of olefins into corresponding naphthenes, either in the noncatalytic process at high temperatures or in the catalytic process at moderate and low temperatures. The formation of a C_5 or C_6 naphthene from an isomeric olefin has not been observed under any conditions. On the other hand, there are many indirect indications of the possibility of such isomerizations. In cracking high molecular weight olefins, the polymerization and decomposition reactions, which have been discussed above, are predominant. The liquid products of cracking, however, particularly the high-boiling fractions, contain various cyclic hydrocarbons, including naphthenes and aromatics. In the presence of aluminum chloride, olefins also produce cyclic hydrocarbons, particularly in high-boiling fractions. It is probable that the formation of naphthenes in all these reactions, catalytic and purely thermal, is a result of various cyclization reactions, and partially of isomerization of certain olefins into corresponding naphthenes.

The catalytic polymerization of olefins under mild temperature conditions yields almost pure polymers. Under more severe conditions of temperature, naphthenes are readily formed as a result of polymerization. The formation of naphthenes in polymerization may be explained either as a result of cyclic isomerization of polymers, primarily formed, or as a direct result of polymerization of olefins into naphthenes under more severe conditions of the process.

Cyclic isomerization of olefins may produce theoretically various types of naphthenes, including the derivatives of cyclohexane and cyclopentane which are largely represented in gasoline fractions.

Naphthenes belonging to the cyclohexane derivatives, formed as a result of cyclic isomerization, can be dehydrogenated to the derivatives of benzene, as will be shown later:



These reactions may explain, at least partially, the occurrence of naphthenes and aromatics in the cracking products of olefins, as well as of paraffins.

A direct cyclization of olefins into aromatics proceeds smoothly in the presence of certain catalysts, as in the case of paraffins. Moldavsky and Kamusher⁸⁵ catalytically transformed normal octene into *o*-xylene and ethylbenzene under the same temperature conditions as normal paraffins.

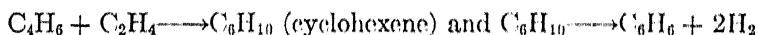
Koch⁷⁶ investigated the aromatization of a heptene fraction. As

catalysts, vanadium and chromic oxides on alumina were used, the temperature being from 440 to 530°C. and the time from 8 to 40 seconds. The highest yield of aromatics, mostly toluene, 37 per cent, was obtained at 510°C. for 40 seconds in the presence of vanadium oxide. In addition to aromatization, the decomposition and condensation reactions occur simultaneously, which deteriorates the catalyst.

The formation of aromatics from such olefins as heptene or octene, as well as from paraffins, may be hypothetically explained on the basis of the same intermediate reactions: paraffins are dehydrogenated into olefins, olefins are isomerized into naphthenes and naphthenes are dehydrogenated into aromatics.

Pitkethly and Steiner^{108b} treated normal heptane with a dehydrogenation catalyst at 475°C. and Hoog and his associates^{54b} treated various paraffins and other hydrocarbons at 465°C. in the presence of chromic oxide. In addition to aromatics, olefins were formed in considerable yields. On the contrary, no naphthenes were detected. It may be probable that the aromatization of paraffins takes place through the intermediate formation of olefins and does not involve the further intermediate formation of cyclohexanes.

Under the conditions of cracking, the formation of aromatics from olefins may be carried out by other reactions than the cyclization of olefins into cyclohexanes and the dehydrogenation of the cyclohexanes formed to aromatics. The aromatics may be produced by the condensation of diolefins with olefins. The reaction takes place through the intermediate formation of cyclic olefins. Butadiene and ethene, for example, may react according to the following equations:



Thus, in the first stage, an olefin and a diolefin are condensed into a cycloolefin which is dehydrogenated in the second reaction. On the other hand, this reaction may be responsible for the formation of cyclic olefins in cracking.

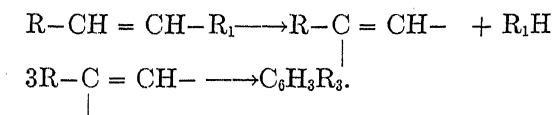
The condensation of butadiene and ethene into cyclohexene is accompanied by a strong decrease in free energy and is easily possible from the thermodynamic standpoint. For instance, ΔF° of this reaction for 227°C. is calculated to be -28,800 cal. It explains a high reactivity of butadiene at the temperatures of cracking.

Wheeler and Wood¹⁴⁰ proved experimentally that butadiene and ethene at 600°C. are combined, forming cyclohexene. On the other hand, 9 per cent by weight of cyclohexene was converted into benzene at 600°C. and 25 per cent at 700°C. Frolic and Schneider⁴⁰ also showed that at 725°C. and 1/5 atmosphere pressure butadiene and ethene produce benzene and hydrogen. According to Schultze,¹¹⁰ butadiene alone, or mixed with ethene or acetylene, readily forms benzene and toluene at 882°C.

Taking into consideration that the thermal treatment of olefins yields

diolefins, it is believed that these reactions between diolefins and olefins may play an important part in the formation of aromatics in cracking.

The old Berthelot acetylene theory is modified by some authors to explain the formation of aromatics from olefins. According to Groll,⁴⁸ "nascent" acetylene and its derivatives are responsible for the formation of aromatics. The olefins are decomposed forming a paraffin and a "nascent" acetylene derivative, which is condensed into a benzene derivative, as follows:



The absence of acetylene and its derivatives in the cracking products of olefins up to 800°C. is explained by the assumption that the "nascent" acetylenes are polymerized to benzene derivatives more readily than they would form an acetylene hydrocarbon.⁴

Thus, different hypothetical sets of reactions may lead to the formation of aromatics from olefins: the cyclization of olefins into cyclohexanes followed by dehydrogenation; the condensation of olefins and diolefins into cycloolefins, followed by dehydrogenation; and the dehydrogenation of olefins to acetylenes, followed by condensation. Other, unknown mechanisms of the transformation of olefins into aromatics also are not improbable. The second set of reactions, *i.e.*, the condensation of olefins and diolefins followed by dehydrogenation, undoubtedly has a better experimental background, but it is not sufficient to cover all phenomena pertaining to the aromatization of olefins, particularly their catalytic aromatization at moderate temperatures.

The aromatization of olefins in the thermal process takes place at comparatively high temperatures. Thus, these reactions occur mostly in the so-called vapor-phase cracking and other processes using temperatures of 600°C. (1112°F.) and higher. Under milder temperature conditions aromatization may take place only to a moderate extent.

In addition to cyclohexene, other cyclic olefins and diolefins are formed, particularly in high-temperature cracking. Frey and Hepp,^{37a} for instance, observed the formation of butadiene and cyclopentadiene in the process of aromatization of butane, evidently through the intermediate formation of olefins. Such cyclic olefins as cyclohexene, cyclopentadiene, etc., are present in vapor-cracked gasolines in appreciable quantities.

Summary of Cracking Reactions of Olefins

Polymerization and depolymerization are the most important cracking reactions of olefins, particularly in the first stage of the process. Polymerization is the predominant reaction at moderately high temperatures and high pressures. At high temperatures of about 600°C. (1112°F.)

and low pressures, depolymerization may be predominant. In more advanced stages of the process the olefins are partially dehydrogenated, forming diolefins, or decomposed forming diolefins and paraffins.

The secondary reactions between olefins and diolefins may produce cyclic olefins. These reactions are responsible for the formation of diolefins and cyclic olefins present in cracked gasolines, usually in comparatively small proportions.

The cyclization of olefins may produce naphthenes. Aromatic hydrocarbons are formed as a result of dehydrogenation of the cycloolefins or naphthenes which were produced in the preceding stages.

The isomerization of olefins, less probable in the thermal process, seems to be a very important reaction in the presence of such catalysts as activated clays.

Commercial Methods of Polymerization of Olefins

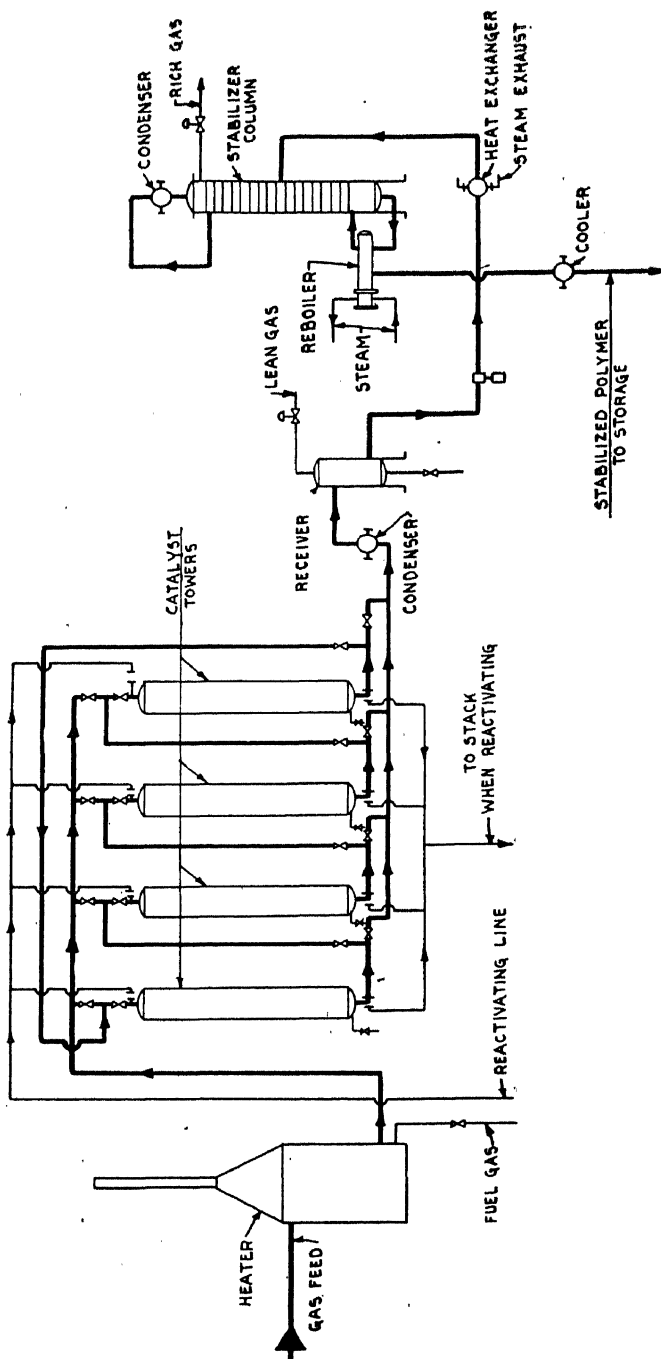
The term "polymerization" is used indiscriminately in petroleum technology, embracing all processes of the production of gasoline from gaseous hydrocarbons. It would be advisable, however, to apply this term only to the true polymerization of olefins. In this case the processes of thermal conversion of hydrocarbon gases into gasoline carried out at high temperatures should be specified as cracking of gases, since the only difference between the conventional cracking of liquid products and that of gases is the state of the stock to be cracked. High-temperature cracking or conversion of gases will be studied in Chapter 2.

The most important commercial process of the polymerization of olefins is the U.O.P. Process using the catalytic action of phosphoric acid, developed by Ipatieff. In the commercial process propene and butene are polymerized to olefinic and naphthenic gasoline, as has been described above. Ethene is polymerized only to a small extent. Propene and butenes are polymerized to 80-95 per cent and ethene to 30 per cent of the original content in olefinic gases. Still cracking gases, stabilizer reflux and stabilizer gases are used as charging stocks for catalytic polymerization. The minimum amount of propene and butenes in the gases should be about 20 per cent.

Phosphoric acid is used on carriers, such as kieselguhr or hydrated alumina. The mixture of catalyst (70-85 per cent) and carrier is calcined at 200-250°C. The phosphoric acid catalyst may gradually lose its activity due to the dehydration of phosphoric acid to inactive metaphosphoric acid. Therefore, a small amount of steam of about 5 per cent is added to the charging stock to prevent dehydration.

The flow diagram of Figure 1b shows that the gases containing olefins are compressed to the pressure of approximately 300-500 pounds per square inch gauge, heated in the tube still to a temperature of 191-204°C. (375-400°F.), and passed through the catalyst chambers in series flow. The chambers are charged with solid granular phosphoric acid catalyst.

The reaction in the catalytic chambers is exothermic, and the tem-



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 1b.—Flow Chart of U.O.P. Catalytic Polymerization Process.

perature of the gases increases to 232-288°C. (450-550°F.), depending upon the percentage of polymerizable olefins. The polymerized and residual gases pass through heat exchangers and coolers. The liquid polymers condensed are stabilized in a stabilizing unit of the conventional type.²⁵

Pressure up to 1100-1200 pounds per square inch and a somewhat lower temperature are used in the latest polymerization units described by Van Voorhis.^{135a} The reaction chamber in these units has two series-connected sets of 16 parallel-connected tubes of 6-inch inside diameter containing a phosphoric acid catalyst. The tubes are all jacketed with 8-inch tubes filled with water to absorb the heat of polymerization. The steam produced is employed for preheating the charge. As can be seen from Figure 2, the charging stock under the above pressure is first preheated in a heat exchanger to 280°F. and then in the steam preheater to 325°F. Thus, all of the heat requirements are provided by the heat of polymerization. The preheated charge enters the first reaction chamber where the temperature is raised to 375°F. and then passes to the second reaction chamber where the temperature increases to 425°F. The drop in pressure in the reaction chambers is about 150 pounds. The pressure is reduced further to 275 pounds per square inch by the pressure control valve before the charge enters the stabilization part of the unit. The charge is first washed with water under a pressure of about 300 pounds for removal of hydrogen sulphide. The yield of polymerized gasoline is about 30 per cent of stabilizer condensed gases containing 42 per cent olefins.

The effect of temperature on the polymerization¹²¹ is demonstrated by the figures of Table 16.

Table 16. Effect of Catalyst Bed Temperature on Olefin Conversion.

Average Bed Temp. (°F.)	Olefin Conversion, (%)	Average Bed Temp. (°F.)	Olefin Conversion, (%)
406	76.5	428	88.3
415	82.0	429	90.0
421	80.5	445	92.2
423	84.4	452	95.0

In addition to temperature and pressure, the time factor in catalytic polymerization—temperature and pressure being constant—influences the yields and properties of the polymerized gasoline.²³ The effect of the

Table 17. Effect of Time Factor on Polymerization Gases.

(Temperature 232°C. (450°F.), Pressure 100-150 Pounds Per Square Inch Gauge).

Operation Conditions:

Contact time, seconds	24	42	65	173
% Polymerization of propene-butenes	70	87	92	99
Yield, gal./1000 cu. ft.	5.6	6.6	7.4	8.4
Gravity, A.P.I. at 60°F.	66.6	67.8	66.4	62.7
Octane number	81	82	80	81
% Distilled over:				
50%, °F.	214	222	234	258
90%, °F.	352	372	420	460
E.P., °F.	411	413	439	531

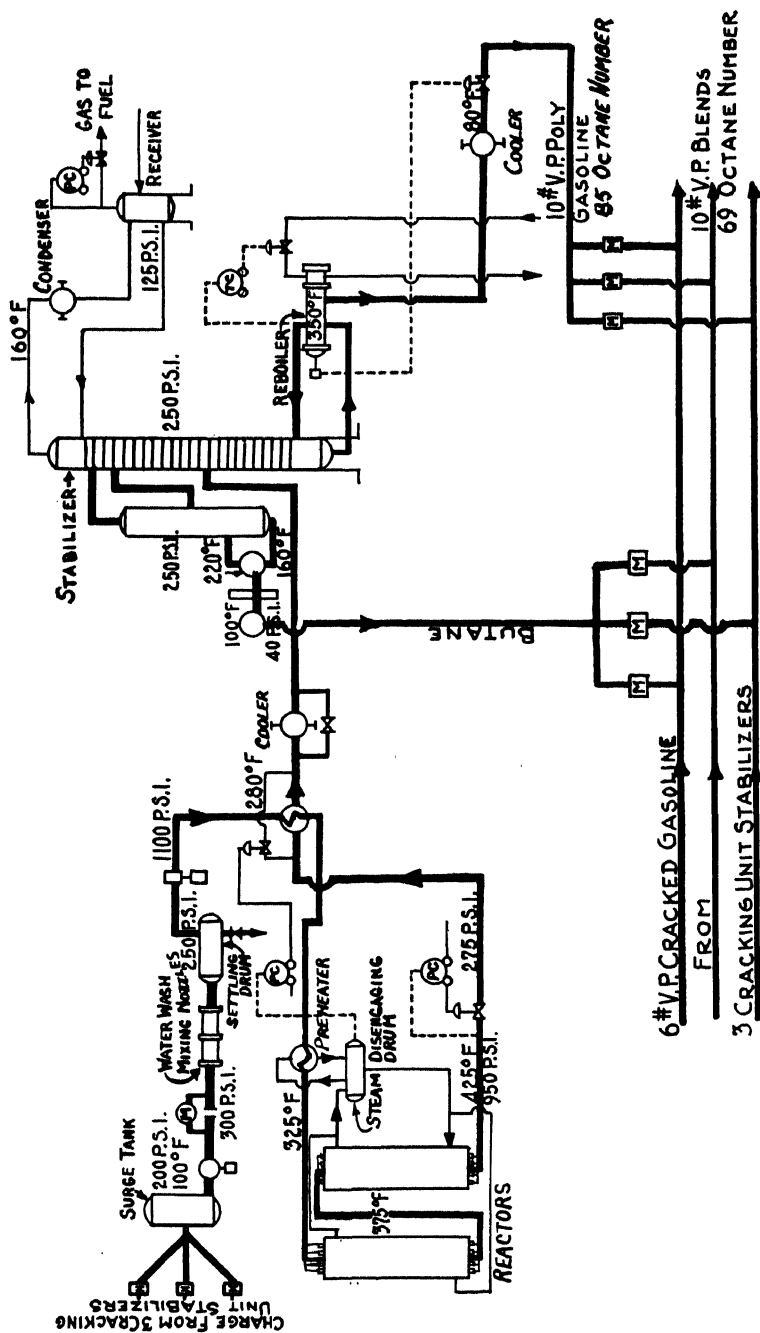


FIGURE 2.—Flow Chart of U.O.P. Catalytic Polymerization Process.

*Courtesy "National Petroleum News"*¹

time on the yields and properties of gasoline is illustrated by the data of Table 17. Thus, the time factor increases the yields of polymerized gasoline, as well as the relative amount of high-boiling fractions.

The extent of polymerization of various olefins is demonstrated by the figures of Table 18.

Table 18. Percentage Conversion of Individual Olefins to Polymerized Gasoline.

Olefin	Plant I	Plant II
Ethene	44	35
Propene	89	98
Butene 1 and 2	71	92
Isobutene	97.3	94
Average % conversion of propene-butenes	85.0	94.9

Thus, propene and isobutene are the most polymerizable constituents, followed by normal butenes and ethene. It should be remembered that in the thermal process ethene is the most polymerizable hydrocarbon.

The yields of polymerized gasoline evidently depend strictly upon the content of polymerizable olefins in gases,²⁷ as shown by the data of Table 19.

Table 19. Yields of Polymerized Gasoline.

Propene and Butenes (% in cracked gas)	Polymerized Gasoline (gals./1000 cu. ft.)	Propene and Butenes (% in cracked gas)	Polymerized Gasoline (gals./1000 cu. ft.)
14.1	2.4	27.1	5.3
17.8	3.0	27.5	5.8
18.0	3.1	33.3	7.0
18.9	3.7	34.3	7.3
21.3	4.2	41.0	9.2
24.1	4.9		

The utilities required for a unit processing 500,000 cubic feet of gas

Fuel	650,000 B.t.u./hour
Water	4,000 gal./hour
Process steam	550 lbs./hour
Compression power	35 H.P.

During operation the catalyst becomes inactive due to the deposition of a carbonaceous material. The working period of the catalyst is about 60 days; after that the catalyst is regenerated by controlled oxidation and subsequent steam treatment for rehydration. As can be seen from Figure 1b the catalytic chambers are arranged so that any one of them may be cut out for regeneration.

Hydrogen sulphide, if present in gases in an appreciable amount, should be removed before polymerization to avoid the difficulties of removing the sulphur compounds from gasoline.

The catalytic polymerization of olefinic gases is a most economical method of converting olefinic gases into gasoline, because of the moderate temperature and pressure used in the process. The initial investment is lower than for thermal conversion. Even the operation of small catalytic polymerization units processing a quarter of a million cubic feet of

cracked gases per day seems to be successful commercially.³³ Only olefinic gases, however, can be processed by the method of catalytic polymerization.

Selective Polymerization of Olefins

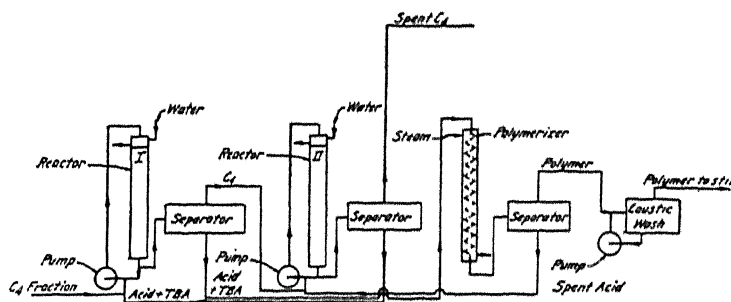
The process described above may be employed for the selective polymerization of isobutene to isoöctene, which is further hydrogenated to commercial isoöctane. As a charging stock, butane-butene fraction of cracked gases is used. The polymerization takes place under relatively mild conditions, under which only or mostly isobutene is polymerized to the dimer and trimer. The yield of polymers amounts to 85 per cent of isobutene. Cotton¹⁷ described the selective polymerization of isobutene by the U.O.P. method in a Gulf Refining Company polymerization plant. The combined polymerization charge contains from 8 to 10 per cent of isobutene. The selective polymerization is carried out at temperatures of 127-171°C. (260-340°F.) and 650-750 pounds per square inch pressure gauge. Diisobutene has an octane number of about 85. After being hydrogenated, diisobutene produces isoöctane having an octane number from 91 to 97, depending upon the yield of polymers. The unpolymerized normal butane and normal butane are used as a blending stock for gasolines.

The Houdry Process Corporation⁵⁵ has developed a selective catalytic polymerization process which is carried out in the presence of activated clay. Polymerization takes place in the liquid phase. The yields of polymers are from 55 to 72 per cent by weight of butenes in one pass. The octane number of polymer gasoline is 84.7 by the A.S.T.M. Motor Method.

More data on the Houdry polymerization process are disclosed in British Patent 503,913 (1939). Polymerization in the presence of activated clay is performed in liquid phase, preferably in the temperature range from 180 to 225°F. The pressure is about 500 pounds per square inch. The rate of feed of the charge is approximately 20 cubic feet of gas per hour per liter of catalyst. The yield of polymers per pass amounts to 40-50 per cent with respect to olefins. The octane number of polymers boiling in the range of gasolines is from 80 to 89 (C.F.R. Motor Method). The period of operation is from 4 to 8 hours, after which the regeneration of the catalyst is carried out, as will be described in Chapter 2.

The catalytic conversion of hydrocarbons in two stages is described in British Patent 505,369 (1939). The polymerization stage takes place under the conditions disclosed above. The unpolymerized hydrocarbons are dehydrogenated at 900-1000°F. and low pressure in the presence of chromium-aluminum oxide catalyst with a contact time of not more than 10 seconds. The olefinic gases formed are returned to the first polymerization stage.

The selective polymerization of isobutene to isoöctene is also performed commercially by reaction with sulphuric acid. There are two modifications of the method: cold and hot processes, described by McAllister.⁸³ In the cold process (Figure 3) the butane-butene fraction is reacted with 60 to 70-per cent sulphuric acid at 20-35°C. counter-currently in two stages. Under these conditions, the action of sulphuric acid is selective, and only isobutene is dissolved in it. As much as 90 per cent of the isobutene may be absorbed by sulphuric acid without appreciably involving the normal butanes. A greater strength of sulphuric acid should be avoided to prevent the polymerization of normal butenes. The acid containing absorbed isobutene is removed from the unreacted portion of the fraction in a separator, and the acid passes into a polymerizer consisting of a coil heated to 100°C. Polymerization is complete



Courtesy "Refiner and Natural Gasoline Manufacture."

FIGURE 3.—Cold-acid Polymerization Plant.

in about a minute, and the products—polymers and sulphuric acid—are separated in the next separator. The polymers contain about 75 per cent diisobutene, the rest being trimers. The hydrogenation of diisobutene produces isoöctane of octane number close to 100.

In the hot modification of the same process, an appreciably higher temperature is used, i.e., from 75-100°C. The concentration of sulphuric acid corresponds to 72 per cent at lower temperatures and to 63 per cent at 100°C. Under these conditions, the rate of polymerization is very high, and the absorption of olefins by sulphuric acid and the polymerization take place in the reactor. No special polymerizer is necessary. On the other hand, under these more severe conditions of treatment, the normal butenes are capable of interpolymerizing with isobutene, forming interpolymers. By this means, the total yield of diisobutenes and interpolymers, as well as the total yield of isoöctane, is considerably increased at the expense of a small decrease in octane number. Table 20 contains comparative results of the cold and hot operations.

Another modification of the process has been suggested by Standard

Oil Development Co. [Br. P. 489, 219 (1938)]. The butane-butene fraction is first subjected to the action of 60-65 per cent sulphuric acid at room temperature to absorb the isobutene, and then to the action of 87-per cent sulphuric acid to absorb *n*-butenes. The two acids are mixed, and the mixture is heated to a temperature of 150 to 300°F. to effect polymerization and copolymerization.

The yield of dimers is reported to be increased and that of trimers to be suppressed by addition of trimers to the polymerizer feed. The amount of added trimer is preferably 2-5 per cent by volume of the polymerizer feed [Standard Oil Development Co., Br. P. 507, 439 (1939)].

Table 20. Polymerization of Butenes by Sulphuric Acid.

	Cold Acid, 65% 30-35°C.	Hot Acid, 65% 80°C.	Hot Acid 65% 90°C.
Composition of Charging Stock:			
Isobutene, % by weight	18.5	18.5	9.1
<i>n</i> -Butene	28.5	28.5	20.6
Butanes	53.5	53.5	70.3
Polymers (%)	17.5	31.4	18.3
Isobutenes polymerized (%)	87.5	100	100
<i>n</i> -Butenes polymerized (%)	5	46	44.5
Total olefins polymerized (%)	37.5	67.5	61.5
O. N. of hydrogenated product	100	99.2	98.8

Commercial Hydrogenation of Isoöctenes

The hydrogenation of isoöctenes is performed commercially either in the low temperature-pressure process with nickel catalyst or in the high pressure-temperature process with sulphur-resistant catalysts.

The low temperature-pressure hydrogenation of isoöctenes¹²² is carried out at temperatures not higher than 200°C. (392°F.) and under moderate pressures below 4 atmospheres. A temperature of 180-190°C. and a pressure of 1 to 4 atmospheres are the most practical conditions. The catalyst consists of activated nickel supported on porcelain.

The catalyst is prepared by impregnation of nickel nitrate in porcelain, decomposing to nickel oxide and reducing to nickel in a stream of hydrogen. The catalyst is very sensitive to sulphur compounds. Before polymerization, the butene fraction is desulphurized, and the octene feed contains on the average 0.0005 per cent sulphur or less. When the catalyst partially loses its activity, it is reactivated *in situ* by oxidation with air and subsequent reduction with hydrogen. The initial activity, however, is not completely restored.

The yield of isoöctane from isoöctene is close to the theoretical (103 per cent versus 105.5 per cent). 1000 gallons of finished isoöctane are produced per one pound of nickel catalyst.

The high temperature-pressure hydrogenation of octenes¹³ is carried out at moderately high temperatures under 200 atmospheres pressure in the presence of high-temperature hydrogenation catalysts (Chapter 3).

The properties of hydrogenated dimers of isobutene and interdimers (codimers) of isobutene and normal butenes are given in Table 21.

Table 21. Properties of Hydrogenated Octenes (High Temperature-Pressure Process)

Property	-Hydrogenated - Dimer	-Hydrogenated - Codimer	Property	-Hydrogenated - Dimer	-Hydrogenated - Codimer
Gravity, A.P.I.	70.9	67.6	A.S.T.M. Distillation		
Color, Saybolt	+30	+30	L.B.P. (°F.)	178	161
Sulphur (%)	0.004	0.006	10%	207	213
Acid Heat (°F.)	2	1	30%	211	222
Bromine No.	3	1	50%	212	224
Octane No., A.S.T.M.			70%	213	227
Motor Method	99	96.5	90%	216	231
			95%	223	234
			E.P.	249	243

The high temperature-pressure hydrogenation catalysts are sulphur-resistant, and the feed is not desulphurized before hydrogenation. The isoöctane produced, however, is almost sulphur-free, due to desulphurization in high-pressure hydrogenation, as will be explained in Chapter 3.

NAPHTHENES

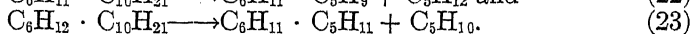
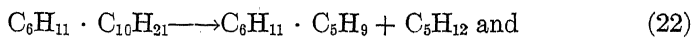
According to the classification accepted in this book, the naphthenes embrace all saturated cyclic hydrocarbons, monocyclic and polycyclic, which have not the aromatic character. The naphthenes of petroleum products are mostly the derivatives of cyclopentane, cyclohexane, Decalin and various other bicyclic as well as tricyclic and tetracyclic naphthenic hydrocarbons of unknown structure. According to Rossini,¹¹⁰ naphthenic rings are frequently combined with aromatic rings with resulting formation of naphtheno-aromatic rings and hydrocarbons. The naphthenes are largely represented in common cracking stocks, such as straight-run gas oils. The proportion of naphthenes in cracking stocks amounts to 60-65 per cent.

Dealkylation of Naphthenes

The paraffinic side chains, frequently very long, are characteristic of the naphthenes of petroleum products. Such naphthenes as cyclopentane, cyclohexane, Decalin, etc., occur in straight-run petroleum products, usually in a very small proportion. The common cracking stocks consist largely of the alkylated naphthenes (or naphtheno-aromatics) with long paraffinic side chains. The length of the paraffinic side chains of naphthenes in cracking stocks depends upon the nature of the crude and the boiling range of the stock. The size of the paraffinic side chains in cracking stocks usually varies from C_5 to C_{15} .

Decomposition of the paraffinic side chains of naphthenes is one of the most important reactions which take place in cracking. The long paraffinic side chains are thermally as unstable as the high molecular weight paraffins. They break down easily at high cracking temperatures, forming either a paraffin and a naphthene with an olefinic side chain, or

an olefin and a naphthene with a paraffinic side chain. For instance, the cracking of the side chain of decylcyclohexane in the middle of the chain may give two reactions:



At the present time, it is impossible to establish which type of decomposition of the side chains is predominant under the cracking conditions.

The break-down of the chains may occur at any carbon-carbon bond, but it occurs for the most part in the middle of the molecule. For this reason, in the first stage of cracking alkylated naphthenes the gas formation, *i.e.*, the formation of low molecular weight hydrocarbons, is very small.

Thus, paraffins and olefins, as well as naphthenes with shorter side chains, are formed as a result of cracking of the side chains of naphthenes. The paraffins and olefins yielded in these reactions are hydrocarbons of the cracked naphtha formed. Part of the naphthenic hydrocarbons with shorter side chains boil in the range of gasolines, but most of them boil in the range of high-boiling fractions, particularly recycle stocks.

The virgin naphthenic hydrocarbons with very long paraffinic side chains (as well as the aromatic and naphtheno-aromatic hydrocarbons with long side chains) are responsible for the high viscosity of high-boiling petroleum fractions. The shortening of the long paraffinic side chains of these hydrocarbons in cracking considerably reduces the viscosity of petroleum products. The well-known "viscosity breaking" of viscous oils and residues is due to the break-down of the long paraffinic side chains in the first stages of cracking.

The splitting of paraffinic side chains may take place in many stages. As a result, the long paraffinic side chain of a naphthene becomes shorter and shorter after several splitting reactions. When the side chain is reduced to an ethyl or methyl group, it becomes comparatively stable and does not undergo any further splitting, unless the temperature-time conditions are extremely severe. Thus, the process of the break-down of the paraffinic side chains may be also designated as the dealkylation process as it shortens the alkyl groups of naphthenic hydrocarbons.

The splitting of side chains, or dealkylation of naphthenes, takes place in the first stages of cracking due to the thermal instability of long paraffinic side chains. The thermal stability of the naphthenic rings is much greater, and the reactions involving chemical changes in the rings, *i.e.*, dehydrogenation and rupture, start later, when the dealkylation reactions are to a great extent completed.

The temperature-time factor of dealkylation of naphthenes should be very close to that of cracking of paraffin hydrocarbons. Thus, the temperature-time conditions governing the cracking of high molecular weight

paraffins (Table 5) should correspond to the conditions of splitting of long paraffinic side chains. As has been mentioned above, the short side chains are comparatively stable. The thermal stability of paraffinic side chains increases with decreasing length of the side chain, as the stability of paraffin hydrocarbons increases with decreasing molecular weight of the hydrocarbon.

Alkylation of Naphthenes

The reverse process of alkylation of naphthenes is similar to that of paraffins. From the thermodynamic standpoint, low temperatures and high pressures are favorable for the alkylation of naphthenes with olefins. As in the case of paraffins, it should be expected that partial alkylation, for instance of cyclopentane or cyclohexane with ethene, in the thermal process might be possible under very high pressures in the neighborhood of 3000 pounds per square inch gauge. Thus, it is not believed that the alkylation reactions of naphthenes with olefins play any part under the more moderate pressures of commercial cracking.

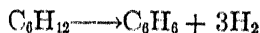
Oberfell and Frey^{64a} alkylated cyclohexane with ethene at 495°C. (923°F.) and 4500 pounds pressure. The yield of ethylcyclohexane was 10 per cent by weight with respect to the charging mixture.

At low temperatures, the alkylation of naphthenes with olefins in the catalytic process may be much more complete than at high temperatures. Ipatieff and his associates⁶⁴ alkylated cyclohexane and its derivatives with ethene at room temperature in the presence of aluminum chloride or boron fluoride. The reaction proceeds under atmospheric or higher pressures. The addition of hydrogen chloride is advisable to activate the catalyst and to prevent the polymerization of olefins. In the presence of zirconium chloride, the alkylation of cyclohexane takes place under pressure at elevated temperatures of 100-150°C. The derivatives of cyclopentane are alkylated under the conditions given above. Only cyclopentane could not be alkylated either with aluminum chloride or with boron fluoride.

Free Energy of Dehydrogenation of Naphthenes

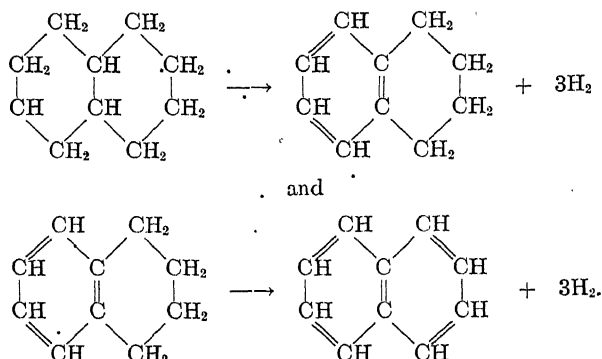
The dehydrogenation of naphthenes is a very important reaction in cracking since it leads to the formation of aromatic hydrocarbons. The naphthenes containing six carbon atoms in the ring, *i.e.*, monocyclic and polycyclic, are very susceptible to dehydrogenation at comparatively high temperatures, particularly in the presence of certain catalysts.

Dehydrogenation of cyclohexane,



proceeds completely to benzene. Any intermediate products of a partial dehydrogenation, as, for instance, cyclohexene, etc., are not formed in this reaction. Polycyclic naphthenes are dehydrogenated according to

the same scheme, but the dehydrogenation of the rings takes place gradually. Decalin, for instance, is dehydrogenated in two stages, as follows:



According to Francis,³⁴ the free energy of the dehydrogenation of cyclohexane to benzene is expressed approximately by the following equation:

$$\Delta F^\circ = 53,700 - 96.6T \quad \Delta F^\circ < 0 \text{ above } 283^\circ\text{C}. \quad (24)$$

The same equation is approximately true for the dehydrogenation of methylhexane.

Equation (24) shows that the dehydrogenation of cyclohexane and its derivatives is probable at temperatures above 300°C ., i.e., in the range of temperatures employed in cracking. The polycyclic naphthenes should have about the same temperature range of dehydrogenation, or even lower.

The dehydrogenation of naphthenes takes place readily in the presence of catalysts at temperatures of 300°C . or higher. In the thermal non-catalytic process only polycyclic naphthenes can be easily dehydrogenated.

Non-catalytic Dehydrogenation of Naphthenes

Cyclohexane is a fairly stable hydrocarbon. Under rather severe conditions, for instance, at 550°C . and 500-700 seconds, it decomposes with the formation of various products, but dehydrogenation to benzene does not occur to any appreciable extent, as the experiments of Pease and Morton show.¹⁰⁶ Frey³⁵ also has found that cyclohexane at 622°C ., 0.7 minute, decomposed to 24.4 per cent, yielded only 0.4 mol per cent of benzene.

However, Terres and his co-workers^{129a} reported on the formation of tetrahydrobenzene, dihydrobenzene and benzene from cyclohexane at temperatures from 600 to 700°C .

According to Dobriansky,¹⁹ the dehydrogenation of alkylated derivatives of cyclohexane takes place more easily; for instance, dimethylcyclohexanes are partially dehydrogenated at temperatures of 480 - 500°C .

As has been mentioned, the polycyclic naphthenes are dehydrogenated

more easily than cyclohexane and its derivatives. Sundgren¹²⁷ investigated the cracking of Tetralin and Decalin at higher temperatures (580-650°C.). Many decomposition products were formed, as well as the products of dehydrogenation. The conditions apparently were too severe for dehydrogenation. Sachanen and Tilicheyev¹²⁸ cracked Tetralin for seven hours at 475°C. In addition to other products formed, the reaction yielded 25 per cent of naphthalene. Decalin at 500°C. and 100 pounds pressure undergoes 95 per cent conversion in 89 minutes, producing benzene, Tetralin, naphthalene and other hydrocarbons (Tilicheyev and Schitikov¹²⁹).

Very little is known of the non-catalytic dehydrogenation of other polycyclic naphthenes. It is very probable that dehydrogenation of the derivatives of Decalin and tricyclic naphthenes proceeds much easier than with Tetralin. Direct experiments on the thermal dehydrogenation of such hydrocarbons are lacking. It is known, however, that naphthalene, methyl and dimethylnaphthalenes and methylated anthracenes may be isolated from the products of the advanced cracking of straight-run gas oils which consist mostly of naphthenes. These aromatic polycyclic hydrocarbons with short side chains are considered to be a result of the dealkylation and dehydrogenation of virgin naphthenes.

Table 22 contains the data on the specific gravities of the fractions of synthetic crudes obtained in cracking Balachany straight-run fuel oil under varied conditions. The fractions of the virgin straight-run Ba-

Table 22.* Specific Gravities at 15°C. of Fractions Obtained from Synthetic Crudes Produced by Cracking Balachany Straight-run Fuel Oil.

Fraction (°C.)	Virgin Fuel Oil	Cracked Residues after Cracking at . . .			
		425°C., 32 Min.	425°C., 92 Min.	425°C., 3 Hours	425°C., 6 Hours
290-350	0.870	0.885	0.900	0.928	0.995
350-375	0.875	0.893	0.909	0.957	1.058 Crystals
375-400	0.885	0.896	0.928	0.961	
400-425	0.892	0.908	0.939	0.975	
425-450	0.900	0.918	0.946	0.982	1.13 Crystals
450-475	0.907	0.924	0.956	0.990	
475-500	0.911	0.928	0.965	1.01	
500-525	0.914	0.930	0.975	1.03	
525-550	0.915	...	0.985	1.05	

* These experiments are described in detail in Chapter 7 and Tables 187-191.

lachany fuel oil consist predominantly of naphthenes insoluble in sulphuric acid. The specific gravities of the fractions markedly and steadily increase with increasing time of cracking, as a result of dealkylation and dehydrogenation (aromatization) of naphthenes. Under the most severe conditions of cracking (425°C., 6 hours), the fractions are entirely aromatic and consist mostly of various crystalline derivatives of anthracene and other polycyclic aromatic hydrocarbons.

The dehydrogenation of naphthenes belonging to the derivatives of cyclohexane and polycyclic six-carbon-ring hydrocarbons is a very important reaction of thermal cracking. As has been stated above, the polycyclic six-carbon-ring naphthenes are readily dehydrogenated, form-

ing corresponding polycyclic aromatic hydrocarbons. The monocyclic cyclohexanes are dehydrogenated with more difficulty, probably only in the advanced stages of cracking. The aromatic hydrocarbons of cracked gasolines and other cracked fractions produced in the mixed phase process are formed mostly as a result of the dehydrogenation of naphthenes present in virgin stocks. The formation of aromatics from olefins, or olefins and diolefins, takes place to a large extent only at high temperatures, for instance, in vapor-phase cracking and other processes using higher temperatures. However, even in vapor-phase cracking, the greater part of the aromatics is due to the dehydrogenation of virgin naphthenes. An easy and smooth formation of aromatic hydrocarbons from naphthenes in cracking explains why naphthenic crudes and products yield more aromatic cracked gasolines than do crudes of paraffinic or mixed bases.

Catalytic Dehydrogenation of Naphthenes

The catalytic dehydrogenation of naphthenes proceeds at moderate temperatures in the presence of various catalysts. The most active dehydrogenation catalysts of mono- and polycyclic naphthenes with six carbons in the rings are palladium, platinum and nickel. The catalysts may be used in powdered form or on carriers, such as charcoal, clay, alumina, etc. In accordance with the thermodynamic conclusions, the dehydrogenation of naphthenes is carried out at temperatures of about 300°C. (572°F.) and at atmospheric pressure. Under these conditions, the process of dehydrogenation is frequently performed quantitatively.

It should be remembered, however, that platinum and nickel catalysts are very sensitive to sulphur compounds, which have to be removed before the dehydrogenation.

Zelinsky¹⁴³ showed that the catalytic dehydrogenation of naphthenes by palladium or platinum is selective, involving only cyclohexane derivatives and those of similar polycyclic hydrocarbons. The temperature should be moderate, not exceeding 300°C. The cyclopentane derivatives are not affected (or give other reactions, as will be shown later) by this reaction and can be separated from the cyclohexane derivatives, and converted into benzene hydrocarbons. The relative amount of cyclohexane and cyclopentane derivatives in gasolines and other products may be determined by this method.

Nickel is another fairly active catalyst for dehydrogenating naphthenes. The process in the presence of this catalyst, however, is accompanied by decomposition reactions, catalyzed by nickel and leading to the formation of methane, carbon and hydrogen. Zelinsky and Komarewsky¹⁴⁵ showed that these undesirable reactions may be considerably suppressed by the use of nickel on alumina or charcoal. According to Gaverdovskaya,⁴² the dehydrogenation action of nickel on alumina or kieselguhr predominates if the concentration of nickel does not exceed 25-30 per cent. At higher concentrations the splitting action of nickel becomes more and more predominant.

The process of catalytic dehydrogenation of cyclohexanes may be used for the commercial production of aromatic hydrocarbons from gasolines which are rich in derivatives of cyclohexane. Zelinsky and Shuykin¹⁴⁷ dehydrogenated some fractions of straight-run Surachany gasolines (boiling range 75-105°C. and 115-125°C.) containing a large proportion of cyclohexane derivatives. The dehydrogenation was performed at 350°C. in the presence of nickel on alumina. As a result, the dehydrogenated fractions contained about 53 per cent of aromatic hydrocarbons.

Some California straight-run gasolines contain as much as 30 per cent of cyclohexanes, and the process in question may be of interest for some selected fractions of these gasolines.

The bicyclic six-carbon-ring naphthenes also are readily dehydrogenated in the presence of catalysts. Zelinsky¹⁴³ dehydrogenated Decalin at 300°C. in the presence of powdered palladium. The products of this reaction consisted only of naphthalene and unchanged Decalin.

Linstead, Millidge, Thomas and Walpole⁷⁸ dehydrogenated quantitatively Tetralin and Decalin, as well as methyl derivatives of Decalin, at 300°C. over platinum and palladium.

Zelinsky, Titz and Fateiew¹⁴⁸ dehydrogenated dicyclohexyl into diphenyl at 300°C. over palladium.

Sabatier and his associates¹¹¹ studied the dehydrogenation of bicyclic naphthenes in the presence of nickel. Over this catalyst Decalin is dehydrogenated to Tetralin at 200°C. and this regenerates naphthalene at 300°C. Over the same catalyst perhydrophenanthrene breaks down at 200°C. into dehydrogenated hydrocarbons and various aliphatic hydrocarbons, while the hexahydride is dehydrogenated to the tetrahydride at 220°C., which in turn regenerates phenanthrene at 280°C. Over nickel at 300-330°C., perhydroanthracene forms the tetrahydride and decomposition products. Decahydrofluorene yields fluorene at 250°C. Thus, the catalytic dehydrogenation of tricyclic naphthenes takes place accompanied by some side reactions of decomposition.

Other catalysts may be employed for the dehydrogenation of naphthenes to aromatics, such as chromium, tungsten and molybdenum compounds. These catalysts require the use of higher temperatures resulting in many side reactions of decomposition. The dehydrogenation of naphthenes cannot be performed quantitatively over these catalysts, as it takes place frequently when platinum or nickel are employed. Clay and silica gel also are mild catalysts for the dehydrogenation of naphthenes. Catalysts of this type, *i.e.*, the metallic oxides and adsorptive materials, are not poisoned in the presence of sulphur compounds. There are some patented processes using such catalysts as the compounds of chromium, tungsten, etc., for dehydrogenation of naphthenes and naphthenic gasolines.

Grosse and Mavity^{49c} used chromic oxide as a catalyst of dehydrogenation. A kerosene fraction (200-250°C.) of Placedo crude was subjected to sulfur dioxide extraction, and the extract produced was dehy-

drogenated over a chromic oxide-alumina catalyst. Substantial quantities of diphenyl- and dimethylnaphthalenes were isolated from the products of dehydrogenation. These hydrocarbons are considered to be a result of dehydrogenation of the dicyclohexyl and dimethyldecahydronaphthalenes present in the virgin kerosene fraction. However, the possible reactions of dealkylation should not be overlooked. The virgin hydrocarbons may be more alkylated than was realized by the authors.

To the author's knowledge, however, no applications of the dehydrogenation of naphthenes to aromatics are used commercially in the oil industry.

Rupture of Naphthenic Rings

The free energy of formation of cyclohexane, ΔF° ,³⁴ is expressed by the following equation:

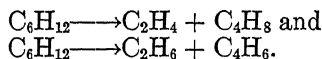
$$\Delta F^\circ = -36,500 + 139.67$$

Thus cyclohexane, as well as other naphthenes, is thermodynamically unstable with respect to the elements at cracking temperatures. Partial decomposition of these hydrocarbons to elements (or methane and elements) may occur at cracking temperatures only in the presence of metallic catalysts and to a very small extent. Usually the rupture of the naphthenic rings yields, not free elements, but some hydrocarbons.

Küchler^{76b} investigated the decomposition of cyclohexane at 497°C. and low pressures. The main decomposition reactions are: (1) dehydrogenation to cyclohexene and hydrogen and (2) decomposition into two molecules of propene. The cyclohexene formed is decomposed further according to the equation:



Two other possible decomposition reactions of cyclohexane are suggested:



The rupture of naphthenic rings takes place under very severe cracking conditions. In this section only the ruptures of monocyclic and bicyclic naphthenic rings are to be discussed; in the case of polycyclic naphthenes rupture usually follows dehydrogenation, and, as a result, the aromatic rings formed break down. It should be remembered that the polycyclic naphthenes are easily dehydrogenated in more advanced stages of cracking.

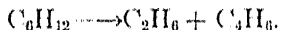
According to Frey,³⁵ cyclopentane is decomposed at 574°C. and 76 mm. pressure for 10 minutes to the extent of 33.5 per cent. The products obtained from cyclopentane under these conditions may partially account for the rupture of the ring according to the equation:



In addition to ethene and propene formed, the decomposition yields the products of partial dehydrogenation of cyclopentane, *i.e.*, C_5H_8 and C_5H_6 .

Zelinsky, Kasansky and Plate¹⁴⁴ showed that cyclopentane may be hydrogenated to open chained normal pentane almost quantitatively under the mild conditions: 300-315°C., atmospheric pressure, platinized charcoal as catalyst. In the absence of hydrogen no reaction occurred under the same conditions of temperature over the same catalyst. Methylcyclopentane was hydrogenated to 2-methylpentane, ethylcyclopentane to isoheptanes, and propylcyclopentane to isoöctanes under the same conditions in the presence of hydrogen.⁷³

Frolich, Simmard and White⁴¹ cracked cyclohexane at 654°C. non-catalytically and obtained butadiene with a yield of 20 per cent on cyclohexane decomposed. Frey³⁵ decomposed cyclohexane to the extent of 43 per cent at 622°C. and 68 mm. pressure for 0.7 min. According to Frey, the products obtained from cyclohexane include low molecular weight olefins and paraffins and cannot be accounted for simply. A considerable formation of butadiene and methylbutadiene should be mentioned, and a partial decomposition of cyclohexane into ethane and butadiene seems to be probable:



Other types of rupture of the ring are responsible for the formation of other hydrocarbons, such as methane, ethene, etc. Destructive hydrogenation of cyclohexane and methylcyclohexane at 400-500°C. in the presence of molybdenum sulphide produces a partial isomerization of the cyclohexane ring into cyclopentane and the formation of paraffins.^{108c}

High yields of butadiene from 34.8 to 41.2 per cent from cyclohexane were reported by Zelinsky, Michailov and Arbusov,¹⁴⁶ when they decomposed cyclohexane, methylcyclohexane and ethylcyclohexane at 750°C. in the presence of 1.5 to 4.0 volumes of water, *i.e.*, under the conditions of a low partial vapor pressure of hydrocarbons. The yields are based on hydrocarbons decomposed.

There are some I. G. Farbenindustrie patents covering the decomposition of cyclohexane and its derivatives into butadiene in the presence of steam and other diluents.

Sundgren¹²⁷ decomposed Tetralin and Decalin at temperatures of 580-650°C. and various pressures. Under these rather severe conditions, benzene and the derivatives of benzene were formed due to the breakdown of one naphthenic ring of the hydrocarbons. The breaking of both rings and ultimate decomposition to methane, carbon and hydrogen increases as the temperature is raised.

Non-catalytic rupture of naphthenic rings occurs under very severe temperature-time conditions. The temperature should be in the neighborhood of 600°C. or higher, under which conditions the naphthenic rings break down. It is hard to expect that the breaking of the rings of mono-

and bicyclic naphthenes might take place to any appreciable extent under the temperature-time conditions of commercial mixed-phase cracking. On the other hand, a partial breakdown of naphthenic rings is probable in vapor-phase cracking at temperatures of about 600°C. and particularly at still higher temperatures.

Isomerization of Naphthenes

Isomerization of the derivatives of cyclopropane and cyclobutane into corresponding olefinic hydrocarbons occurs easily in the presence of some catalysts. These reactions, however, are beyond the scope of this book due to the minor importance of these cycloparaffins to petroleum stocks. Only the isomerization of cyclopentane and cyclohexane and their derivatives is discussed in this section.

According to equation (21), the isomerization of cyclohexane, and probably cyclopentane, into corresponding olefins is thermodynamically possible at temperatures above 540°C. However, the olefins which might be formed as a result of this isomerization are unstable at such high temperatures and may be decomposed further, yielding olefins of low molecular weight, or diolefins and paraffins. These reactions of the rupture of naphthenic rings have been discussed in the previous section.

It has been accepted from the standpoint of Bayer's strain theory that the six-carbon naphthenic ring is less stable than the five-carbon ring. The isomerization of the derivatives of cyclohexane into those of cyclopentane seemed to confirm this theory. A classic example is the isomerization of cyclohexane into methylcyclopentane under the action of certain catalysts, such as aluminum chloride or acids.^{1a}

This conception is in disagreement with the new data of Nenitzescu and Cantuniaru.⁹¹ These investigators studied the isomerization of cyclohexane into methylcyclopentane and the reverse process of isomerization of methylcyclopentane into cyclohexane in the presence of aluminum chloride, containing water for activation. The temperature of the reaction was 70°C. They found that there is an equilibrium between these two hydrocarbons, and that the equilibrium mixture contains only 22.8 per cent methylcyclopentane. Glazebrook and Lovell⁴⁵ confirmed the results obtained by Nenitzescu and Cantuniaru. They found that the equilibrium between cyclohexane and methylcyclopentane depends greatly upon the temperature: the mol per cent of methylcyclopentane in the equilibrium mixture increases from 12.5 at 25°C. to 25.6 at 77.4°C. According to Prokopetz *et al.*,^{108d} cyclohexane is isomerized at 500°C. in the presence of molybdenum and nickel sulphide yielding methylcyclohexane, and under the same conditions the methylcyclohexane is partially isomerized into cyclohexane.⁹ These data are in a fair agreement with the latest thermodynamic calculations of Moore and Parks,^{87d} according to which ΔF° for the isomerization of cyclohexane to methylcyclopentane is +950 cal. Pines and Ipatieff^{108a} showed that the

alkylated cyclopentanes are isomerized to the derivatives of cyclohexane in the presence of aluminum chloride to the extent of 80 per cent.

Zelinsky and Turova-Pollak¹⁴⁰ have shown that Decalin is isomerized, probably into dimethylbicyclooctane, in the presence of aluminum chloride or hydrogen iodide. The process is evidently analogous to the isomerization of cyclohexane. The investigation of Jones and Linstead⁷¹ supports the mechanism of isomerization suggested by Zelinsky.

Grignard and Stratford⁴⁷ have discovered another type of isomerization of naphthenes. Such derivatives of cyclohexane as ethyl, normal and isopropyl, and various butyl and amyl cyclohexanes, are isomerized in the presence of aluminum chloride mostly into methylated derivatives of cyclohexane. The temperature is from 120 to 150°C. Under these conditions, isomerization is accompanied by cracking of some heavier side chains, particularly amyl groups.

The various types of isomerization of naphthenes studied up to the present time are catalytic processes, taking place mostly in the presence of aluminum chloride. The possible extent of these reactions in non-catalytic thermal cracking is quite unknown.

Summary of Cracking Reactions of Naphthenes

The predominant reactions in the cracking of naphthenes are dealkylation (splitting of paraffinic side chains) and dehydrogenation to aromatic hydrocarbons; these can proceed simultaneously. It is understood that only naphthenes of the six-carbon-ring structure are subjected to dehydrogenation. Dealkylation, involving unstable, long paraffinic side chains, takes place in the first stages of cracking. As cracking proceeds, the naphthenes are gradually transformed to naphthenes or aromatics having comparatively short side chains. Very short side chains, particularly methyl and ethyl groups, being thermally stable, are not subjected to further dealkylation under the conditions of commercial cracking. The paraffinic side chains split to form paraffins and olefins of gas and other low-boiling cracking fractions in addition to low molecular weight monocyclic naphthenes and dealkylated aromatics.

In the first and medium stages of cracking the dealkylated naphthenes preserve the ring structure of the virgin naphthenic hydrocarbons due to the great thermal stability of the cyclopentane and cyclohexane rings. In the very advanced stages of cracking or in high-temperature processes rupture of the naphthenic rings may occur to a certain extent, resulting in annihilation of ring structure or in partial decyclization of polycyclic structures.

AROMATIC HYDROCARBONS

The aromatic hydrocarbons of petroleum products belong to the derivatives of benzene and polycyclic aromatics. According to Rossini,¹¹⁰ in high-boiling fractions of mid-continent crudes, polycyclic hydrocarbons

are composed of molecules having either 3 aromatic rings and 1 naphthenic ring, 2 aromatic rings and 2 naphthenic rings, or 1 aromatic ring and 1, 2, or 3 naphthenic rings.

The relative amount of the aromatic hydrocarbons in cracking stocks depends upon the nature of the crude and the boiling range of the stock. High-boiling cracking stocks from asphaltic crudes may contain as much as 30 per cent aromatic hydrocarbons absorbed by sulphuric acid. The common gas oils of Mid-continent contain about 15 per cent aromatics. The aromatic hydrocarbons of straight-run products, particularly of high boiling range, have long paraffinic side chains.

The part played by the aromatic hydrocarbons in cracking is much more important than might first be expected. It should be remembered that aromatics are formed to a great extent in cracking by dehydrogenation of naphthenes. This process, accompanied by simultaneous dealkylation, largely produces aromatic hydrocarbons having comparatively short side chains. The recycling stocks may contain up to 30 per cent and more of aromatics and unsaturates absorbed by sulphuric acid.

Dealkylation of Aromatic Hydrocarbons

The long paraffinic side chains of aromatic hydrocarbons are thermally as unstable as those of naphthenes. They split up in the first stages of cracking, and, as a result, aromatics with shorter side chains are formed according to equations (22) and (23). All conclusions made with respect to the dealkylation of naphthenes may be applied to that of aromatic hydrocarbons. In addition to aromatics having shorter side chains, paraffins and olefins are formed as a result of dealkylation. As in the case of naphthenes, dealkylation of high-boiling and viscous aromatics having long side chains "breaks down" the viscosity. The degree of instability of long paraffinic side chains depends mostly on the size of the chain and does not depend on the aromatic ring, being practically the same for the derivatives of benzene, naphthalene and other polycyclic aromatics.

Dobriansky and his associates^{19a} investigated the cracking of the derivatives of benzene with short side chains: ethyl, isopropyl, butyl, tertiary butyl, amyl and iso-amyl benzenes. The temperature of cracking was from 600-650°C. The following conclusions can be drawn: (1) Hydrocarbons with benzene ring attached to the primary carbon atom of the paraffinic side chain yield toluene and styrene; (2) those with benzene ring attached to the secondary carbon atom form mainly styrene; (3) those with benzene ring attached to the tertiary carbon atom yield mainly benzene. This investigation shows that both types of the decomposition of side chains mentioned above (equations 22 and 23) may occur under cracking conditions.

Ipatieff and Pines^{67a} studied the catalytic dealkylation of various benzene derivatives from toluene to butylbenzenes at temperatures of 350 to 400°C. in the presence of hydrogen. The paraffinic side chains break

down at various carbon-to-carbon bonds. For example, *n*-butylbenzene produces ethylbenzene, toluene and benzene.

Laidler and Szayna^{70c} studied the destructive hydrogenation of phenyl-*n*-octadecane at high temperatures under 110 atmospheres initial hydrogen pressure. At 440°C., for 1 hour, only the paraffinic side chain was broken, forming smaller, mostly liquid, hydrocarbons, partially as free paraffins and partially as low molecular weight derivatives of benzene. The total amount of phenyl groups in fractions obtained was 22.4 per cent, *i.e.*, the same as in the initial hydrocarbon. Thus, under the above conditions, the benzene ring is completely stable. At 470°C., for 1 hour, the total amount of phenyl groups was only 17.4 per cent, almost one-third being mainly hydrogenated to the naphthenic ring. At 490°C., for 1 hour, approximately 15.85 per cent of phenyl groups was found in the reaction products. A very large decomposition to gas took place under these rather severe conditions.

An approximately equal rate of decomposition of paraffins and paraffinic side chains of cyclic hydrocarbons having the same number of carbon atoms may be illustrated by the data of Laidler and Szayna on the destructive hydrogenation of octadecane and phenyl-*n*-octadecane. At 440°C., for 1 hour, *n*-octadecane formed 85.6 per cent liquids, mostly paraffin hydrocarbons. Under the same conditions, phenyl-*n*-octadecane gave 91 per cent liquid products including 22 per cent phenyl groups. Thus, the percentage of paraffin liquid products and paraffinic side chains, combined with the phenyl groups, is 69 per cent. The percentage recalculated on the basis of *n*-octadecyl gives 89 per cent, the figure being very close to that for the hydrogenation of *n*-octadecane. A similar recalculation for the destructive hydrogenation of phenyl-*n*-octadecane at 490°C., for 1 hour, gives a figure very close to that for the hydrogenation of *n*-octadecane.

The breakdown of paraffinic side chains takes place at every carbon-carbon bond but predominantly in the middle of the side chains, as in the case of paraffinic hydrocarbons. The aforementioned investigation of Laidler and Szayna shows that in the destructive hydrogenation of phenyl-*n*-octadecane at 440°C., for 1 hour, the phenyl groups are present mostly in the high-boiling cracked fractions obtained, distilling above 200°C.; in other words, the phenyl groups are combined with comparatively long side chains (more than C₅). Under more severe conditions at 470°C., for 1 hour, the phenyl groups of the cracked fractions are combined mostly with methyl, ethyl, propyl and butyl radicals (fractions from 70-200°C.), as a result of the further splitting of the alkylated benzenes formed in the first stage of the process. Finally, under the most severe conditions used at 490°C., for 1 hour, benzene, toluene and ethyl benzene predominate. It should be noticed that the temperature-time factor of commercial cracking is close to that of the first experiment at 440°C., for 1 hour.

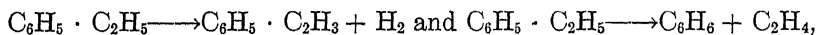
It is of importance that the dealkylation of aromatics is accompanied

by some condensation reactions. Sachanen and Tilicheyev¹¹³ partially dealkylated cymene mainly to toluene and xylenes at 425°C. and 90 atmospheres pressure for 3 hours. The extent of dealkylation under these conditions was comparatively small, and only 4.1 per cent toluene and xylenes were formed, in addition to 6.2 per cent high-boiling fractions containing the condensation products. Similar results were observed under more severe cracking conditions.

The alkyl aromatics boiling in the range from 150 to 250°C. and consisting predominantly of propyl, amyl and heptylbenzenes, sp. gr. 0.860, were cracked at 482°C. (900°F.) and 50 atmospheres pressure for 40 minutes. As a result of cracking, 43.5 per cent almost unchanged alkyl benzenes, sp. gr. 0.872, were recovered, in addition to 25 per cent dealkylation products, mostly toluene and xylenes, 10.5 per cent gases and light gasolines, 15 per cent liquid condensation products of sp. gr. 1.04, and 6 per cent coke and asphaltic materials. Thus, the extent of dealkylation (25 per cent dealkylated benzenes) corresponds closely to that of condensation reactions (21 per cent liquid condensation products and coke). The condensation reactions are due to the secondary reactions between aromatics or aromatics and olefins formed, as will be shown in the next section.

The alkylated aromatics with short paraffinic side chains are thermally stable, particularly the derivatives of benzene.

Pease and Morton¹⁰⁶ investigated the decomposition of benzene and its derivatives at 630°C. It is of interest that at this temperature *o*-xylene and toluene seem to be more stable than benzene itself, forming a lesser amount of gas. The stability of *m*-xylene is of the same order as that of benzene. Ethyl benzene is much less stable, yielding as much gas at 550°C. as does benzene at 630°C. The authors suggest that the dealkylation of ethylbenzene may take place in two directions:



the first reaction (formation of styrene) being predominant.

It is of interest that at high temperatures even ethylbenzene is more stable than cyclohexane. The thermal stability of aromatics with short side chains exceeds that of all other hydrocarbons of about the same number of carbon atoms, including cyclopentane and cyclohexane.

According to Zalkind and Bulavsky,¹⁴¹ the formation of styrene from ethylbenzene may be practically quantitative. At 660-670°C. ethylbenzene diluted with nitrogen and under low pressure yields 82.7 per cent styrene.

Methylated naphthalenes are less stable than methylated benzenes. According to Tilicheyev and Schitikov,¹³¹ methylnaphthalenes are partially dealkylated at 450-475°C., yielding naphthalene, and dimethylnaphthalenes are dealkylated at the same temperatures producing β -methylnaphthalene. The last hydrocarbon is thermally more stable

than the α -isomer. However, these reactions of demethylation of alkyl naphthalenes, as well as of other aromatics, may take place only in very advanced stages of cracking under rather severe conditions of temperature and time. Under the conditions of commercial cracking, such alkylated aromatics as methyl and ethyl benzenes, methyl and ethyl naphthalenes, etc., are quite stable and are not subjected to further dealkylation to any appreciable extent. Commercial cracking does not produce completely dealkylated aromatic hydrocarbons, such as benzene, naphthalene and anthracene.

The aromatic rings are much more stable than the paraffinic side chains. As a result, the processes of dealkylation of aromatics, at least at the temperatures of commercial cracking, proceed smoothly without breaking the ring structure of the dealkylated aromatics. In the advanced stages of cracking the dealkylated aromatics are partially condensed to polycyclic hydrocarbons.

The dealkylation of aromatics having long paraffinic side chains is one of the most important reactions of cracking, leading to the formation of low molecular weight paraffins, olefins and aromatics with shorter side chains.

Alkylation of Aromatic Hydrocarbons

Alkylation of aromatic hydrocarbons takes place much more easily than that of paraffins and naphthenes. The free energy of alkylation of aromatics can be calculated for the reaction of benzene with ethene, forming *m*-xylene:

$$\Delta F^\circ = -26,000 + 32T. \quad (25)$$

Thus, the free energy of alkylation of aromatics is more negative than that of paraffins (equation 11). It remains negative at high temperatures up to 540°C. (1000°F.). Thus, thermal alkylation of aromatics can occur in a rather broad temperature range and under lower pressures than alkylation of paraffins.

As a matter of fact, benzene or toluene can be partially alkylated with olefins at temperatures of 400-500°C. and at pressures of about 100 atmospheres in a purely thermal process. The process may be carried out more efficiently in the presence of various catalysts. With activated clay, for instance, alkylation of benzene with olefins takes place at moderate temperatures and pressures, giving high yields of alkylated benzenes. Schollkopf^{118a} alkylated naphthalene with ethene at 230°C. under 20-40 atmospheres' pressure in the presence of an activated hydro-silicate catalyst.

In the presence of more active catalysts alkylation of aromatics may be carried out at low temperatures. In the presence of phosphoric acid⁶⁴ benzene is alkylated with isobutene at 60°C., naphthalene with propene at 200°C. under pressure, and fluorene with propene at 120°C. under a

pressure of 10-15 atmospheres. Phosphorus pentoxide alkylates aromatic hydrocarbons under similar conditions.⁷⁹

Such agents as sulphuric acid or aluminum chloride alkylate benzene with olefins at room temperature. According to Reid and his associates,⁵ alkylation of benzene with ethene in the presence of aluminum chloride forms a whole series of ethylated benzenes, including hexaethylbenzene. The amount of aluminum chloride used is about 1 mol per 13 mols of benzene.

The action of sulphuric acid is similar to that of aluminum chloride but is less energetic.⁶⁴ Ethene does not react with benzene in the presence of sulphuric acid, but other olefins readily form mono-, di-, and trialkylated benzenes. A comparatively large amount of sulphuric acid must be used for the reaction.

Other metallic chlorides, such as ferric, zirconium, tantalum and zinc chlorides, may be used for the alkylation of benzene and other aromatics.

The alkylation of naphthalene, anthracene and other aromatics with olefins in the presence of aluminum chloride has been covered by many patents of I. G. Farbenindustrie.⁶⁹ Simons and Archer^{123a} found that hydrogen fluoride promotes the alkylation of benzene with olefins at such a low temperature as 0°C. Tinker and Weinmayr^{133a} alkylated benzene and naphthalene with propene by this method and obtained high yields of mono- and polyalkylated derivatives.

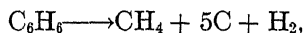
The alkylation of aromatics with olefins in cracking may play a more important part than other types of alkylation. Some low molecular weight derivatives of benzene formed as a result of cracking may be alkylated with olefins under conditions of high pressure. The catalytic action of clay used in some modern cracking processes is a factor very favorable to the alkylation of benzene hydrocarbons.

Rupture and Condensation of Aromatic Rings

The free energy of formation of benzene and naphthalene³⁴ is expressed by the following equations:

$$\text{Benzene } \Delta F^\circ = 17,200 + 43T \quad \text{Naphthalene } \Delta F^\circ = 28,600 + 66T$$

As can be seen from these equations, aromatic hydrocarbons are thermodynamically unstable with reference to the elements at all temperatures, including those of cracking. The decomposition reactions of aromatic hydrocarbons into methane and elements, such as for instance:



have positive values of free energy and also are thermodynamically possible. As in the case of other hydrocarbons, these reactions, leading to the rupture of the aromatic rings, practically never occur in thermal cracking. In the presence of such catalysts as nickel, however, these reactions may take place easily at comparatively moderate temperatures. Zanetty and Egloff¹⁴² found, for instance, that at 500°C. the gas and carbon formation

from benzene was only 1 per cent in the thermal process and 36 per cent in the presence of nickel, other conditions being equal.

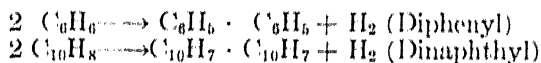
Baneroft and Genge² investigated the decomposition of benzene in the presence of hydrogen and nickel catalyst at temperatures of 250 to 300°C. At 300°C. benzene is readily decomposed to methane with complete rupture of the ring.

According to Zanetty and Egloff,^{1,2} at temperatures above 750°C. benzene is directly decomposed into carbon and hydrogen, the reactions of the direct decomposition being predominant over the condensation reactions under these temperature conditions. It should be mentioned, however, that in the thermal experiments (without catalyst) the relative amount of the condensation products (diphenyl and tar) is considerably larger than that of gas and coke even at 750-800°C. (34 per cent *versus* 16 per cent at 800°C.). At least a part of the coke formed may be considered as a result of further condensation of the tar. On the other hand, the direct decomposition of benzene into gas and carbon in the presence of metallic catalysts seems to be certain.

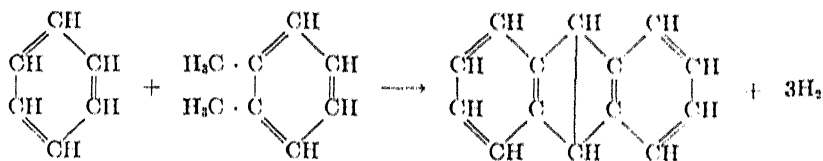
Thus, the rupture of the aromatic rings almost never occurs under the conditions of commercial cracking in the absence of specific catalysts. The reactions of the condensation of aromatic rings are of greater importance and readily occur in cracking.

The condensation of aromatics, particularly polycyclic, takes place readily at high temperatures. It leads to the formation of more and more polycyclic structures, poor in hydrogen. The last stage of condensation is the formation of asphaltenes and coke, highly carbonaceous compounds, very polycyclic and poor in hydrogen.

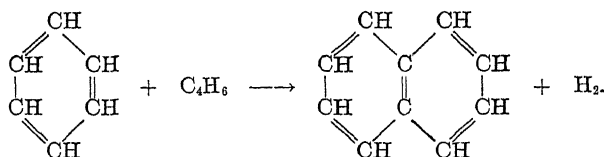
There are various types of aromatic condensation at cracking temperatures. The simplest and best-known is the reaction between two molecules of an aromatic forming a corresponding diaromatic, as for instance:



Condensation of this type, however, occurs in cracking only to a comparatively small extent, as will be shown in this paragraph. The condensation through two carbon atoms, leading to the formation of more condensed polycyclic rings, such as naphthalene, anthracene, phenanthrene, etc., is a more common phenomenon. This condensation may take place in many ways, for instance between two molecules of aromatics



or between an aromatic and an olefin (diolefin):



Many condensations of these types were reported in the early investigations of Berthelot,⁶ Barbier,³ Ferko³² and others, as for instance, the formation of anthracene and phenanthrene from benzene and ethene, naphthalene and ethene, diphenylmethane, etc., at high temperatures.

The free energy of the condensation reactions has negative values at cracking temperatures. For instance, ΔF° of the aforementioned condensation of benzene and butadiene to naphthalene may be expressed by the following equation:

$$\Delta F^\circ = -12,800 - 13.4T \quad (26)$$

Thus, the free energy of this reaction is slightly negative at low temperatures and strongly negative at cracking temperatures.

The exact mechanism of the formation of polycyclic rings, condensed through two carbon atoms, remains rather obscure. Probably both reactions of the condensation, *i.e.*, between aromatics and an aromatic and an olefin, occur under the conditions of cracking.

Benzene is very stable with respect to condensation. At 500°C. and higher, benzene is partially condensed to diphenyl. The yields of diphenyl formed, however, are small, not exceeding 3-5 per cent, if the temperature is below 600°C. Under more severe temperature conditions, for example in high-temperature aromatization, other condensations of benzene readily occur. Notwithstanding a great number of investigations, the mechanism of high-temperature condensations of benzene, above 600°C., is not quite clear. In addition to diphenyl, other polycyclic aromatics are formed, including diphenylbenzenes, and still more polycyclic aromatic hydrocarbons. Naphthalene is absent in the products of high-temperature cracking of benzene.

The ability of the derivatives of benzene to take part in condensation reactions is much greater than that of benzene itself. Toluene and xylenes are condensed to diphenyl, naphthalene, anthracene, dibenzyl, ditolyl and others at temperatures of 600°C. and higher. These methylated derivatives of benzene, as well as benzene itself, should be considered as fairly stable at the temperatures of commercial cracking in mixed or vapor phase processes, not exceeding 600°C.

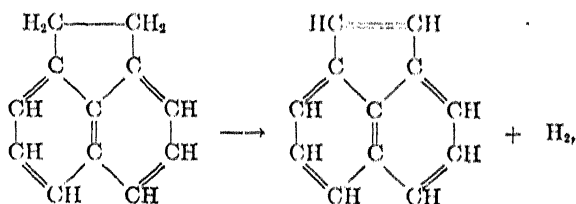
The high molecular derivatives of benzene are less stable, being condensed with formation of naphthalene derivatives and other polycyclic aromatics. As has been described above, dealkylation of benzene derivatives boiling between 150 and 250°C., at 482°C. (900°F.), produced almost as many condensation products as did dealkylated aromatics (toluene and xylenes).

The thermal stability of the naphthalene-ring also is very high. Cracking at 475°C. for 4 hours and 20 minutes produced but a very slight action: only about 1.5 per cent of dinaphthyl was formed. No coke and no products of lower boiling range were observed.¹¹³ According to Tilicheyev and Schitikov,¹³¹ the methyl derivatives of naphthalene are condensed, with direct linking of two rings, the rings being combined together through a $-\text{CH}_2\text{CH}_2-$ bridge. In addition to this type of condensation, asphaltenes are readily formed as a result of the condensation of many naphthalene rings through two carbon atoms.

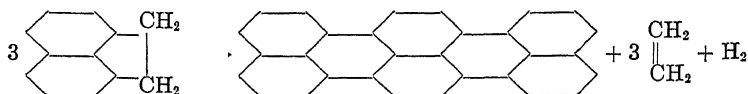
The rupture of one ring of naphthalene and its derivatives, with formation of the derivatives of benzene, does not take place to any large extent even at such high temperatures as 600-700°C. At these temperatures and various pressures (from 1 to 14 atmospheres) Egloff²⁴ decomposed an oil containing mostly the derivatives of naphthalene. The yields of benzene and toluene were from 1.4 to 5 per cent with respect to the original oil. It is evident that the formation of benzene derivatives from those of naphthalene should be entirely absent under the milder conditions of commercial cracking.

Diphenyl is approximately as stable as naphthalene, but the condensation stability of diphenylmethane and triphenylmethane is much lower. According to Tilicheyev and Schitikov,¹³³ the time required for the formation of 1 per cent of coke at 500°C. for diphenyl, diphenylmethane and triphenylmethane are 3,600-310 and 34 minutes, respectively. Fluorene is close to triphenylmethane (the time of 1 per cent coke formation at 500°C. is 51 minutes). Some decomposition reactions accompany the condensation processes, resulting in the formation of benzene and toluene. The aromatic hydrocarbons mentioned above are 10 per cent decomposed at 500°C. in 106, 7.5, 4.4 and 2.3 minutes respectively. Thus there is a certain relationship between the rates of decomposition and condensation.

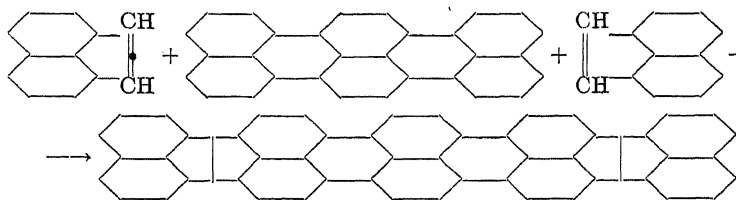
The condensation of acenaphthene was studied by Dzievonsky.²¹ Unfortunately, the temperature of the reaction was not measured; it was conducted in a quartz tube filled with copper or iron turnings, heated at red heat. The temperature of the reaction may be computed very approximately as between 550 and 600°C. The flow of acenaphthene with carbon dioxide was rather rapid, and the time of the reaction should be comparatively short. In addition to the well-known dehydrogenation of acenaphthene to acenaphthylene:



Dzievonsky observed the condensation of acenaphthene and acenaphthylene to more polycyclic aromatic hydrocarbons. According to Dzievonsky, the formation of rhodacene (or isomeric chalcacene) corresponds to the following condensation:



Rhodacene is condensed further with the acenaphthylene formed, yielding leukacene:



About 25 per cent unchanged acenaphthene was recovered; the yield of acenaphthylene was about 60 per cent and that of the above-mentioned and some other condensation products was about 15 per cent of the acenaphthene used.

Rhodacene, chalcacene and leukacene are crystalline compounds, which can be purified by crystallization from various solvents. The highly condensed compounds mentioned above and the probable reactions of their formation, illustrating very clearly the course of the condensation processes of aromatic hydrocarbons, are of particular interest from the standpoint of cracking.

Dzievonsky and Suszko,²² working under the same conditions, condensed fluorene into various polycyclic aromatics containing 7 benzene and cyclopentyl rings.

The tricyclic aromatic hydrocarbons, such as anthracene and phenanthrene, are condensed very easily under cracking conditions. Anthracene cracked at 475°C. for 3½ hours was completely transformed to coke containing 59 per cent carbon insoluble in benzene.¹¹³ According to Tili-cheyev and Schitikov,¹³² phenanthrene is more stable than anthracene. The relative rates of coke formation at 500°C. for naphthalene, phenanthrene and anthracene are as follows: 1:78:10,800. The rates of cracking of these hydrocarbons follow approximately the general rule, increasing around two times per 10°C.

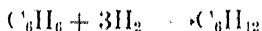
The difference in condensation reactions and in coke formation between bicyclic and polycyclic aromatic hydrocarbons should be kept in mind. While naphthalene and diphenyl at 500°C. for many hours yield only an insignificant amount of condensation products, anthracene, and to a lesser extent phenanthrene, are transformed to coke under the same conditions. The boiling range of the derivatives of tricyclic aromatic hydrocarbons is above 360°C. (680°F.), whereas the derivatives of bicyclic aromatics

distill below this temperature, if the paraffinic side chains are not too long. Thus, the fractions boiling below 360°C. (680°F.) should have much less coke formation in cracking as compared with the fractions boiling above this temperature, consisting predominantly of the derivatives of tricyclic aromatics. The difference in the coke-forming properties of anthracene and phenanthrene derivatives should be also kept in mind.

The condensation reactions of aromatic hydrocarbons are of primary importance in cracking. They occur as a result of the condensation of two or many molecules of aromatics or of aromatics with olefins. The polycyclic aromatics are particularly likely to condense. The condensed aromatic hydrocarbons may be converted into coke in more advanced stages of cracking, as will be shown in Chapter 2.

Hydrogenation of Aromatic Hydrocarbons

The free energy of hydrogenation of benzene and toluene²⁴



is expressed by the following equation:

$$\Delta F^\circ = -53,700 + 96.67' \quad \Delta F^\circ < 0 \text{ below } 285^\circ\text{C}. \quad (27)$$

High pressures of hydrogen favor the reaction; the following equation represents a shift in the free energy, if the hydrogen pressure is increased to P atmospheres:

$$\Delta F = -3RT \log \text{nat } P \quad (28)$$

The free energy of hydrogenation of benzene, ΔF° , is negative at low temperatures up to 285°C. (545°F.). Thus, thermodynamically hydrogenation of aromatics is possible at low temperatures under atmospheric pressure. On the other hand, hydrogenation is possible at high temperatures, but under high hydrogen pressures. For instance, equation (28) shows that the free energy of hydrogenation of benzene is zero at 500°C. and 100 atmospheres' pressure, and negative under higher pressures. Thus, the hydrogenation of aromatics can proceed at 500°C. and even higher, if the hydrogen pressure is above 100 atmospheres. The higher the temperature, the higher should be the hydrogen pressure to effect hydrogenation.

The rate of hydrogenation increases with increasing hydrogen pressure. The use of catalysts is another important factor in hydrogenation. As in the case of dehydrogenation, platinum, palladium and nickel are the most powerful catalysts; they are very sensitive, however, to sulphur compounds. Hydrogenation catalysts which are resistant to sulphur include oxides and sulphides of molybdenum, chromium, tungsten, and some other metals.

The low-temperature hydrogenation of aromatics takes place only in the presence of catalysts. Such catalysts as platinum and nickel are much more active at low temperatures than the sulphur-resistant catalysts.

A high pressure of hydrogen may not be used in low-temperature hydrogenation, but it enormously enhances the rate of hydrogenation. At low and moderate temperatures of the process, hydrogenation of aromatics is the predominant reaction, and decomposition reactions do not occur to any appreciable extent. As a result, the cyclic or polycyclic structure of the hydrogenated aromatic is the same as that of the virgin aromatic hydrocarbon. This process may be specified as non-destructive hydrogenation of aromatics.

As has been disclosed above, high-temperature hydrogenation is possible only under high hydrogen pressures. The reaction is usually performed catalytically, but for the polycyclic aromatics the process may be carried out in the absence of catalysts. Under high temperature conditions, many decomposition reactions occur, in addition to the hydrogenation. The extent of the decomposition evidently depends upon the temperature and time of the reaction. The process is designated as destructive hydrogenation. The decomposition reactions taking place in destructive hydrogenation may be either the splitting of paraffinic side chains or the decyclization of aromatic rings. The first reaction has been discussed above, and the last reaction, which is very important to the process in question, will be discussed in detail later.

The border between low-temperature (non-destructive) and high-temperature (destructive) hydrogenation of aromatics is not quite definite and depends upon many factors, including the nature of the aromatics, the time of reaction, etc. Very stable benzene may be hydrogenated at a high temperature, such as 450°C. and higher, without any appreciable decomposition. For polycyclic aromatic hydrocarbons the upper temperature limit of non-destructive hydrogenation is much lower, in the neighborhood of 400-425°C., but the extent of decomposition at high temperatures may be controlled by the use of short reaction times. Destructive hydrogenation is carried out at temperatures above 450°C.

Non-destructive Hydrogenation of Aromatic Hydrocarbons

Benzene is the most inactive aromatic with respect to hydrogenation. In the absence of catalysts, benzene cannot be hydrogenated at 485°C. and 250 atmospheres for 3 hours. Under approximately the same conditions, toluene is partially converted into benzene (50 per cent), also without hydrogenation of the ring. Even in the presence of molybdenum catalysts, benzene, toluene and xylene were not hydrogenated at 400-450°C. and 65-100 atmospheres of initial hydrogen pressure for 3 hours.⁶² However, Prokopetz *et al.*^{108c} hydrogenated benzene over molybdenum sulphide on kaolin at a temperature of 450°C. and 200 atm. pressure, the contact time being 1.6 minutes.

Pure copper prepared from precipitated hydroxide, being inactive at ordinary pressures, catalyzes the hydrogenation of benzene under superatmospheric pressures. The hydrogenating activity of copper is largely dependent upon the presence of impurities, particularly of nickel. Thus,

copper containing 0.1 per cent of nickel oxide readily catalyzes the hydrogenation of benzene under atmospheric pressure.^{64a}

Nickel catalyst is much more active. Sabatier and Senderens¹¹¹ hydrogenated benzene into cyclohexane in the presence of nickel at a temperature of 110-190°C. under atmospheric pressure.

According to Ipatieff,⁶² benzene may be effectively hydrogenated under high pressures of hydrogen. Benzene was converted to cyclohexane in the presence of nickel oxide, at 250°C. and 100-120 atmospheres of initial hydrogen pressure, for 2-3 hours.

Diakova, Losovoy and Stepanitzeva¹⁸ hydrogenated with a nickel catalyst various derivatives of benzene, including xylenes, hexamethylbenzene and others. The temperature was from 200 to 240°C., the working pressure from 120 to 230 atmospheres. Hydrogenation was almost complete. The reaction was not accompanied by any splitting of side chains. The derivatives of benzene are hydrogenated more easily than benzene itself with the exception of hexamethylbenzene. The size and structure of the paraffinic side chains (from toluene to octylbenzene) does not cause any marked difference in the rate of hydrogenation. On the contrary, the number of paraffinic side chains greatly decreases the rate of hydrogenation.¹⁸

The polycyclic aromatic hydrocarbons are hydrogenated still more easily, as compared with benzene derivatives.

Sabatier and his associates¹¹¹ hydrogenated polycyclic aromatics in the presence of nickel under atmospheric pressure. Naphthalene produced Decalin at 175°C.; while at 200°C. hydrogenation is not complete and Tetralin is formed. Anthracene forms perhydroanthracene at 180°C., octo-hydride at 200°C. and tetrahydride at 260°C.

Ipatieff hydrogenated naphthalene to Tetralin and Decalin, diphenyl to dicyclohexyl, etc., at 250°C. and 100-120 atmospheres of initial hydrogen pressure in the presence of nickel oxide.

The polycyclic aromatics can be hydrogenated under high pressure even in the absence of catalysts. Spilker and Zerbe¹²⁴ non-catalytically hydrogenated naphthalene mostly to Tetralin at 440-470°C. and 75-100 atmospheres of initial hydrogen pressure for 3 hours. Anthracene, phenanthrene and acenaphthene were hydrogenated at 450°C. and 75-80 atmospheres of initial hydrogen pressure to corresponding hydrogenated derivatives, octo- and tetrahydroanthracenes, tetrahydrophenanthrene and tetrahydronaphthacene. Fluorene was hydrogenated at 465°C. The temperatures used were a little too high for non-destructive hydrogenation, and some decomposition reactions took place to a small extent.

Catalytic hydrogenation of benzene is performed in one stage. It is transformed directly into cyclohexane without intermediate formation of cyclohexene. The hydrogenation of polycyclic aromatics takes place in consecutive stages, *i.e.*, the rings are hydrogenated in consecutive order. Each ring, however, is hydrogenated completely, as in the case of benzene. This phenomenon, discovered by Sabatier and Senderens, was investigated

more thoroughly by Waterman and his associates. Waterman, Clausen and Tulleners¹³⁸ hydrogenated naphthalene in the presence of nickel on kieselguhr at 180-300°C., the initial hydrogen pressure being about 100 atmospheres. The hydrogenation took place readily, and tetrahydronaphthalene was formed. It was impossible, however, to continue hydrogenation further. New catalyst had to be added to convert Tetralin into Decalin in further hydrogenation.

Hydrogenation of anthracene¹³⁹ in the presence of the same catalyst produces readily octohydroanthracene at 180-220°C., the time of reaction being 3-4 hours. When this stage was reached, the hydrogenation rate decreased greatly, and further hydrogenation of octohydroanthracene to perhydroanthracene was carried out after the addition of new catalyst.

The analogy between catalytic hydrogenation and dehydrogenation should be mentioned. The aromatic rings are hydrogenated and hydroaromatic rings are dehydrogenated completely, without formation of partially hydrogenated rings. With polycyclic hydrocarbons both processes take place in a number of consecutive stages, corresponding to the number of cycles.

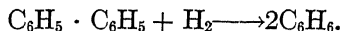
Destructive Hydrogenation of Aromatic Hydrocarbons

Destructive catalytic hydrogenation of benzene first produces cyclohexane which is partially isomerized into methylcyclopentane. The cyclohexane and cyclopentane formed may decompose in further stages of hydrogenation, yielding open chain paraffins. However, the mechanism of these reactions is unknown.

Destructive hydrogenation of some derivatives of benzene was studied by Waterman and his associates.^{10b} In the presence of a nickel catalyst the derivatives of benzene, being destructively hydrogenated at temperatures above 450°C., produce partially dealkylated benzenes, naphthenes and paraffins.

Destructive high-pressure hydrogenation of polycyclic aromatics above 450°C. is one of the most important reactions in commercial hydrogenation of petroleum products. The general mechanism of destructive hydrogenation may be summarized as a decondensation or degradation of polycyclic aromatic rings. As a result, polycyclic aromatic hydrocarbons are transformed to more simple ones, down to the derivatives of benzene.

According to Hofmann and Lang,⁵³ diphenyl at 500°C. and 200 atmospheres hydrogen pressure is converted into benzene to the extent of 92.3 per cent:



The reaction is reversible, and at 485°C. and 250 atmospheres pressure benzene forms 1-2 per cent diphenyl. In any case, the equilibrium at 500°C. and 200 atmospheres pressure is almost entirely shifted to the side of benzene. The reaction is non-catalytic.

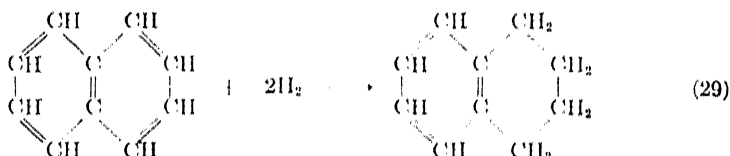
Szayna¹²⁸ studied the hydrogenation of diphenyl at 480°C., the time of the reaction being 70 minutes and the initial hydrogen pressure 115 atmospheres. Molybdenum sulphide was used as a catalyst. The reaction formed 25.3 per cent of decyclization products, consisting of benzene (15 per cent), cyclohexane (6 per cent) and cyclopentane (4 per cent).

Ipatieff and Kliukwin^{66a} found that naphthalene at 450-480°C. and 100 atmospheres initial hydrogen pressure for 25-30 hours formed about 15 per cent benzene hydrocarbons, in addition to Tetralin. Nickel on alumina was used as catalyst.

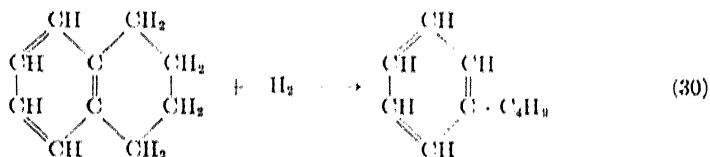
Kling and Florentin⁷⁵ studied the hydrogenation of naphthalene at temperatures of 400-500°C. and found a considerable formation of benzene derivatives in the presence of small amounts of aluminum chloride.

According to Jeru,⁷⁹ under more severe conditions at 510°C. and 122 atmospheres hydrogen pressure, naphthalene produces as much as 50 per cent of the derivatives of benzene boiling up to 140°C. The hydrogenation was carried out with molybdenum as catalyst.

As these investigations clearly show, the process of destructive hydrogenation of naphthalene takes place in two stages, the first stage being the partial hydrogenation of naphthalene to Tetralin:

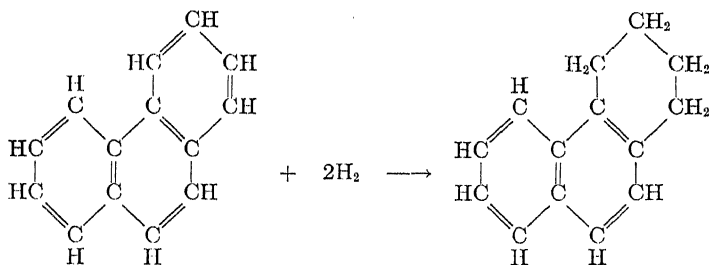


Tetralin is thermally much more unstable than naphthalene due to the presence of a polymethylene ring. It decomposes in the second stage of hydrogenation, breaking in the polymethylene ring according to the equation:

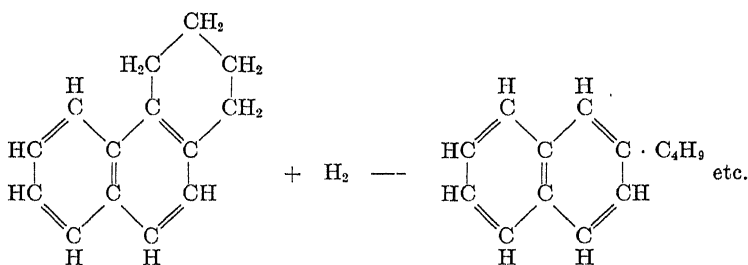


It is understood that the decomposition may be accompanied by dealkylation, leading to the formation of such benzene derivatives as ethylbenzene and toluene.

Destructive hydrogenation of phenanthrene was performed by Orlov^{95, 96} at 450-500°C. and 70-75 atmospheres initial hydrogen pressure in the presence of CuO, NiO and FeO on alumina. After 14 hours the following compounds were formed: toluene, xylenes, naphthalene, methyl and ethyl naphthalenes and dihydrophenanthrene. If the conditions were more severe (40-48 hours), the benzene derivatives were almost single products of the process. The hydrogenation of phenanthrene to dihydro- or tetrahydrophenanthrene is considered as a first stage of hydrogenation:



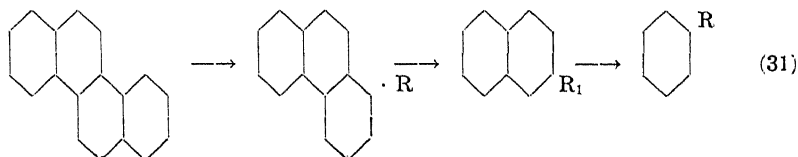
The tetrahydrophenanthrene, like Tetralin, is thermally unstable and forms naphthalene derivatives which in turn are decyclized to benzene derivatives:



Anthracene at 400°C. and 120 atmospheres initial hydrogen pressure yields various hydrogenated derivatives from tetrahydroanthracene to perhydroanthracene.⁹⁸ At this temperature the hydrogenated anthracenes are comparatively stable, and the hydrogenation is predominant, as has been found by Spilker and Zerbe. At 480°C. and the same hydrogen pressure, low-boiling products are formed. The mechanism of destructive hydrogenation is similar to that in the previous reactions. The tetrahydroanthracene formed breaks down in the hydrogenated ring, yielding derivatives of naphthalene, which are partially hydrogenated to derivatives of Tetralin. The latter breaks down in the same way, yielding derivatives of benzene.

Fluorene⁹⁶ at 460-470°C. and 75 atmospheres initial hydrogen pressure for 15-20 hours forms mostly derivatives of benzene, as a result of the decomposition of the tetrahydrofluorene formed in the first stage of the process.

Orlov and Lichatshev⁹⁷ studied the hydrogenation of chrysene. At 440-450°C. and 100 atmospheres initial hydrogen pressure for 26 hours, chrysene forms a series of decyclization products, according to the following scheme:

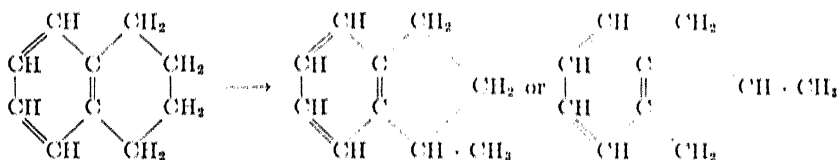


Thus, the mechanism of destructive hydrogenation of all polycyclic aromatic hydrocarbons is the same. As a result, the polycyclic aromatics are decondensed or degraded. The reverse condensation reactions of aromatic hydrocarbons, taking place under the same temperature conditions in cracking, are suppressed and replaced by decondensation reactions.

Isomerization of Aromatic Hydrocarbons

The isomerization of aromatics at high temperatures may proceed in various ways but there are no definite data on the occurrence of these reactions in cracking. The isomerization due to the shift of a paraffinic side chain along the aromatic ring appears to be possible even in the thermal non-catalytic process. *Ortho* and *para* isomers of the substituted benzenes are less stable than *meta* isomers, and α -substituted naphthalenes are less stable than β -isomers. Thus, the isomerization of alkyl derivatives of benzene and naphthalenes into *meta*- and β -derivatives respectively should be expected under cracking conditions.

The isomerization of aromatic rings has a particular interest. Orlov and Lichatshev⁹⁸ cracked Tetralin non-catalytically in the presence of hydrogen at 460-470°C. for 4-6 hours. The reaction produced about 50 per cent of low-boiling fractions. The fractions boiling in the range 170-195°C. were carefully fractionated and gave a series of fractions boiling between 180 and 192°C. The latter were sulphonated and converted into sodium sulphonate. The sodium sulphonate after purification was converted with sulphuric acid and steam into a hydrocarbon, which was identified as methylhydroinden. The isomerization is represented by the following:



It is of interest that the thermal conditions of the isomerization in question correspond closely to those of commercial cracking.

In an earlier work Orlov⁹⁵ observed partial isomerization of phenanthrene to anthracene when he conducted the vapors of phenanthrene with hydrogen through a copper tube heated to a temperature not exceeding 750°C.

Summary of Cracking Reactions of Aromatic Hydrocarbons

The main cracking reactions of aromatic hydrocarbons are dealkylation (splitting of paraffinic side chains) and condensation. The dealkylation produces paraffins, olefins and aromatic hydrocarbons with short side chains. The aromatics with such paraffinic groups as methyl, ethyl, etc., are comparatively stable under customary cracking conditions and

do not undergo further dealkylation, unless the temperature is particularly high.

The condensation of aromatics takes place either between aromatics and aromatics or between aromatics and olefins (or other unsaturates). As a result, polycyclic aromatic hydrocarbons are formed which may be condensed further to asphaltic compounds and coke.

In commercial hydrogenation condensation reactions do not occur. On the contrary, the reverse reactions of decyclization of polycyclic aromatics take place under the conditions of high temperature-high pressure hydrogenation.

SUMMARY OF CRACKING REACTIONS OF HYDROCARBONS

The cracking reactions of all hydrocarbons which may be present in cracking stocks (both straight-run and recycle) are summarized in Table 23.

The scheme clearly shows the general trend of cracking reactions. Paraffins undergo mostly the splitting (and dehydrogenation) reactions, gradually producing hydrocarbons of lower and lower molecular weight. Olefins are polymerized and partially decomposed in the first stage of cracking, but are decomposed mainly in the further stages, with formation of olefins, paraffins and diolefins. Cyclic olefins may be produced as a result of the reactions between olefins and diolefins. The isomerization of olefins may produce naphthenes. Aromatics are formed from cycloolefins and naphthenes by dehydrogenation.

Naphthenes and aromatics in the first stage of the process are mostly dealkylated, forming paraffins, olefins and dealkylated naphthenes and aromatics with shorter side chains. Naphthenes are further dehydrogenated to aromatics. Aromatics are largely subjected to condensation reactions, yielding polycyclic aromatic hydrocarbons which form coke in the advanced stages of cracking.

The scheme shows clearly that coke formation is a secondary reaction taking place readily in cracking aromatic hydrocarbons. In cracking paraffins and olefins, coke formation is a result of a series of preceding intermediate reactions.

In destructive hydrogenation the condensation of aromatic hydrocarbons is suppressed, and the reverse reactions of decyclization occur to a great extent, forming in the final steps the derivatives of benzene.

The fact that many hydrocarbons of petroleum products are actually combinations of various types of hydrocarbons does not change considerably the above general scheme of cracking. The cracking of a hydrocarbon, including different structures in the molecule, proceeds in every structural part of the molecule to a certain degree, independently of the other structural parts. For instance, the long paraffinic side chains of naphthenes or aromatics split as they would if they were paraffin hydrocarbons of about the same number of carbon atoms. The ring structure

of the naphthene or aromatic is not changed in this process of dealkylation or splitting of paraffinic side chains. The dehydrogenation of the ring takes place usually after the partial dealkylation.

OXYGEN, SULPHUR AND NITROGEN COMPOUNDS

As was stated in the beginning of this chapter, the total percentage of the non-hydrocarbon constituents in gas oils usually does not exceed 1 per cent. On the other hand, the content of these compounds in heavy asphaltic residues may be as high as 10 per cent and more, up to 30-50 per cent, depending upon the nature of the crude and the percentage of overhead distillates. Thus, the part played by the non-hydrocarbon compounds in cracking may be very significant for certain residual stocks.

Naphthenic Acids

The low and medium molecular weight oxygen compounds of petroleum products belong mostly to the group of acids specified as commercial naphthenic acids. The relative amount of the naphthenic acids in some crudes, according to the data of Shipp,¹²³ is given in Table 24.

Table 24. Naphthenic Acid Content in Various Crudes.

Crude	Naphthenic Acid Content, % by Weight	Crude	Naphthenic Acid Content, % by Weight
Texas, Winkler	0.30	California, So. Calif. and San Joaquin Valley	0.1-3.0
Texas, Howard	0.07	Baku, Balachany light	1.05
Texas, Runnels	0.03	Baku, Balachany heavy	1.10
Louisiana, Horston	0.70	Baku, Binagady heavy	0.85
Michigan, Saginaw	0.03	Baku, Bibi-Eibat, light	0.55
Arkansas, Smackover	0.03	Baku, Bibi-Eibat, heavy	0.50
M. C., pipe line	0.04	Baku, Ramany	0.40
Pennsylvania	0.03	Baku, Surachany	0.20
Gulf Coast	0.60	Grozny, mixed base*	0.20
		Grozny, asphalt base	0.5-0.8

* The data for Grozny oils are supplemented by the author.

The content of naphthenic acids in common charging cracking stocks, such as gas oils, is usually small, from 0.01 to 0.04 per cent in Pennsylvania and Mid-continent distillates, and from 0.3 to 0.4 per cent in California and Gulf products.

The commercial naphthenic acids extracted from crudes or distillates by alkaline solutions may contain phenols, aliphatic carboxylic acids and the naphthenic acids proper.

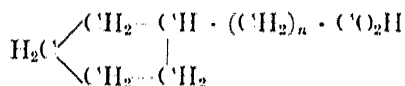
It is believed that the content of phenols in crudes and straight-run products is very small, but in some cases the phenols make up an appreciable part of commercial naphthenic acids, as has been found by Holzmänn and von Pilat⁵⁴ for a Boryslav kerosene. As phenols, cresols, xyenols and naphthols were detected in straight-run products.

Phenols are comparatively stable under moderate temperature conditions of cracking and may remain, at least partially, undecomposed in

cracking. Apparently the content of phenols in cracked products is greater than in virgin cracking stocks. If so, the phenols of cracked products should be formed at the expense of other oxygen derivatives, perhaps resinous and asphaltic compounds.

The content of aliphatic carboxylic acids in petroleum products also is very small. Mostly low molecular weight aliphatic acids were detected in commercial naphthenic acids.

Cyclic carboxylic acids or naphthenic acids make up the bulk of commercial naphthenic acids. The chemical structure of the naphthenic acids was finally cleared up by von Braun.¹¹ The naphthenic acids consist predominantly of the carboxylic acids of the derivatives of cyclopentane in which the carboxylic group links to a paraffinic side chain, as for instance:



The cyclopentane ring of the naphthenic acids is more or less highly alkylated. The high molecular weight naphthenic acids may also belong to the derivatives of a double naphthenic ring. The acids with $n = 1$ predominate. The naphthenic acids with a direct linking of the carboxylic group to the ring ($n = 0$) occur much less frequently.

Cracking of naphthenic acids has not been studied thoroughly. Dry distillation of the salts of naphthenic acids produced hydrocarbons and probably ketones.⁴⁶ The pressure cracking of naphthenic acids in the presence of water was investigated by Ipatieff and Petrov⁶⁷ at 400°C. for 5 hours. The following decomposition reactions of naphthenic acids were suggested: (1) The formation of naphthenes due to the scission of carboxylic groups. (2) The formation of naphthenic acids of a lower molecular weight owing to the splitting of paraffinic side chains. (3) The formation of paraffins and low molecular weight paraffin carboxylic acids, as a result of the splitting of paraffinic side chains and side chains containing a carboxyl group.

Sulphur Compounds

The relative amount of sulphur compounds depends upon the nature of the crude, as the data of Table 145 clearly show. The content of sulphur in the fractions of a crude increases from gasoline to residuum, as can be seen from the data of Perkin¹⁰⁷ given in Table 25.

These data show that the amount of sulphur may be considerable in heavy distillates and residues of certain crudes.

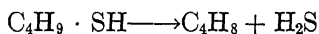
The sulphur compounds present in straight-run products belong to various classes, including hydrogen sulphide, mercaptans, mono- and disulphides and thiophenes. In addition to these compounds, crudes contain the resinous and asphaltic ingredients which are the compounds of

Table 25. Sulphur Content of Fractions of Crudes.

Fraction (°C.) American Crude, Sulphur 0.72%—	Sulphur (%)	Fraction (°C.) —Canada (Petrolia), Sulphur— 0.98–1.01%	Sulphur (%)
to 90	0.02		
110–150	0.10	115–150	0.28
150–220	0.38	150–200	0.42
220–257	0.41	200–250	0.50
257–300	0.37	250–300	0.51
300–350	0.37	300–350	0.86
Residuum	0.54	Residuum	0.70

oxygen and sulphur and which are present mostly in high-boiling fractions and residues.

The cracking of low and medium molecular weight sulphur compounds was investigated by Faragher, Morrell and Comay,³⁰ Elgin,²⁹ Malisof and Marks⁸⁰ and others. The general results of these investigations may be summarized as follows. The most stable organic compounds of sulphur are mercaptans and thiophenes. Sulphides and disulphides under cracking conditions form mostly elemental sulphur, hydrogen sulphide and mercaptans. The mercaptans in the further stages of cracking yield hydrogen sulphide and olefins, as for example



The last reaction is reversible, and at lower temperatures and in the presence of some catalysts, such as nickel sulphide, clay and silica gel, an olefin and hydrogen sulphide yield a mercaptan.

Resins and Asphaltenes

As has been mentioned above, other oxygen and sulphur compounds of petroleum products contain both elements. These compounds, neutral resins, asphaltenes and asphaltogenic acids, frequently occur in high-boiling distillates and residues in considerable quantities. They are highly polycyclic compounds with short side chains. According to Marcusson,⁸¹ the oxygen and sulphur atoms of these compounds are present in the "bridges," *i.e.*, in the middle of rings, and link two opposite carbon atoms of the ring. The content of oxygen in the neutral resins and asphaltenes ranges from 5 to 10 per cent and that of sulphur from 0.5 to 5 per cent. When a petroleum product is hydrogenated, the resins and asphaltenes are transformed to hydrocarbons, oxygen and sulphur being reduced to water and hydrogen sulphide. On the other hand, the neutral resins and asphaltenes may be formed from high molecular polycyclic hydrocarbons by oxidation. These reactions show that there is a very close connection between polycyclic hydrocarbons and neutral resins and asphaltenes. It should be mentioned that the oxidation of paraffinic hydrocarbons or long paraffinic side chains produces predominantly acids, whereas neutral resinous products are formed by the oxidation of aromatics.

The asphaltenes are precipitated by petroleum ether, and the neutral

resins can be extracted after the removal of asphaltenes by various adsorbents, such as silica gel or floridin.

The neutral resins *ipso facto* are not soluble in aqueous or alcohol alkaline solutions. They are volatile and are present in all fractions with the exception of gasolines. The color of oil distillates is mostly due to the neutral resins which are of an intense dark red color. The molecular weight of a neutral resin is close to that of the fraction from which the resin was extracted. Table 26 contains the data on the occurrence and formulas of the neutral resins extracted from various fractions of a Grozny crude, according to Sachanen and Vassilieff.¹¹⁸ Thus, the neutral

Table 26. Content of Neutral Resins and Asphaltenes in Fractions of a Grozny Crude, Sp. Gr. 0.870 (31.1 A.P.I.).

Fraction	Specific Gravity at 20°C.	Content of Neutral Resins (%)	Content of Asphaltenes (%)	Average Formula of Neutral Resin*
Crude	0.870	8.24		$C_{41}H_{58}O_2$
Kerosene	0.811	0.07		$C_{19}H_{30}O_2$
Gas oil	0.878	0.57		$C_{22}H_{32}O_2$
Neutral, 250 Saybolt at 122°F.	0.930	5.81		$C_{32}H_{46}O_2$
Neutral, 550 Saybolt at 122°F.	0.957	7.38	0.11	$C_{32}H_{46}O_2$
Residuum	0.978	21.3	13.0	$C_{63}H_{72}O_3$

* Sulphur present in neutral resins is included in oxygen.

resins occurring in some heavy distillates in considerable amount may play an important part in cracking.

The asphaltenes are colloidal products which are present in oil products in colloidal solution due to peptization by resins and other soluble polycyclic aromatic constituents. They are lyophobic to paraffin hydrocarbons and such solvents as petroleum ether, and coagulate in the presence of these solvents.¹¹² The molecular weight of asphaltenes is high, amounting to many thousands. Asphaltenes are formed by the oxidation of neutral resins at moderate temperatures. The content of asphaltenes in heavy crudes and residues varies from traces (in Pennsylvania crude and residues) to 10 per cent and more in heavy asphaltic residual products. Asphaltenes are non-volatile and absent in freshly distilled distillates. There is a close connection between neutral resins and asphaltenes which have the same polycyclic structure.

According to Nellensteyn,⁸⁹ the asphaltenes and similar asphaltic products consist of ultramicroscopic and microscopic particles of elemental carbon protected by resins and highly unsaturated hydrocarbons, often with a high content of sulphur. This hypothesis should be considered as highly improbable. As has been stated above, neutral resins are transformed into asphaltenes very easily even at room temperature or at slightly elevated temperatures. The formation of elemental carbon from the neutral resins at low temperatures seems to be hardly probable. On the other hand, the neutral resins may be distilled without decomposition, so that the existence of elemental carbon in these compounds cannot be postulated. The gradual condensation of aromatic hydrocarbons at high temperatures, leading to the formation of highly polycyclic hydro-

carbons, asphaltic compounds and coke, is also inconsistent with Nellensteyn's hypothesis of elemental carbon.

The asphaltogenic acids are similar to asphaltenes but have an acidic character. These compounds, present in cracking stocks in very insignificant amounts, are of no importance in cracking reactions.

Cracking of neutral resins and asphaltenes produces gases, liquid products and a large amount of coke. The yield of coke from asphaltenes is about 60 per cent by weight and from neutral resins from 7 to 20 per cent, depending upon the molecular weight of resins. The high molecular resins give greater yields of coke. The gaseous and liquid cracking products of neutral resins and asphaltenes have not been studied. The cracking of these compounds may be of interest as a source of the oxygen and sulphur derivatives present in cracked products.

Cracking of heavy asphaltic crudes and residues containing a large amount of neutral resins and asphaltenes produces large yields of coke. Distillation of these charging stocks and cracking of the distillates reduce considerably the coke formation due to the elimination of asphaltenes and reduction in the content of neutral resins.

Nitrogen Compounds

The content of nitrogen compounds in crudes and cracking stocks is usually considerably less than that of sulphur derivatives. The content of nitrogen in most crudes does not exceed 0.01-0.1 per cent and only in a few oils (*e.g.*, some California crudes), is it close to 0.5 per cent. The distribution of nitrogen compounds in the fractions is the same as of sulphur compounds, *i.e.*, the content of nitrogen increases with increasing boiling range of the fraction.

The nitrogen compounds present in oils belong to the derivatives of organic nitrogen bases, aliphatic and aromatic, investigated by Mabery and later by Bailey and his associates.¹⁰

Nothing is known of the cracking of these compounds. The presence of some derivatives of pyridine and other nitrogen bases in cracked products shows that the nitrogen bases may be cracked without rupture of the ring containing nitrogen.

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Chapter 2

Fundamental Factors of Cracking

CRACKING STOCKS AND PRODUCTS

Cracking is the thermal or catalytic-thermal treatment of petroleum products at temperatures higher than 400°C . (752°F .). The decomposition as well as the condensation reactions proceed under these temperature conditions. Thus, the term "cracking" embracing only decomposition reactions is not quite adequate to denote the whole variety of cracking phenomena.

During the earlier years of the commercial development of cracking, only high-boiling products, such as kerosene, gas oils and residues, were used as charging stocks for cracking. At the present time the list of cracking stocks includes gasoline and hydrocarbon gases, in other words, practically all petroleum products. The sole difference between the cracking of gases and of liquid oil products is the reversed value of the condensation or polymerization reactions. In cracking liquid products, the decomposition reactions leading to the formation of gasoline are the most important from the commercial standpoint. The condensation and polymerization reactions, forming products of low commercial value, are controlled and allowed to proceed to the minimum extent. In cracking gases, the decomposition reactions lead to the formation of olefins which are polymerized and condensed to the liquid hydrocarbons boiling in the range of gasolines.

As a result of cracking, a variety of cracked products is formed, beginning with hydrogen and gaseous hydrocarbons and ending with high molecular weight condensation products. The condensation products may include asphaltic compounds and coke. Gasoline, the main product of commercial processes, is one of the various products of cracking.

The following example gives a clear idea of the various distillates formed in cracking. A narrow lubricating oil fraction, boiling between 250 and 285°C . at 6 mm. pressure, of specific gravity 0.910, was cracked in a bomb at 425°C . for 64 minutes (pressure at the end of the experiment 72 atmospheres). The results of distillation of the cracked product are given in Table 27.

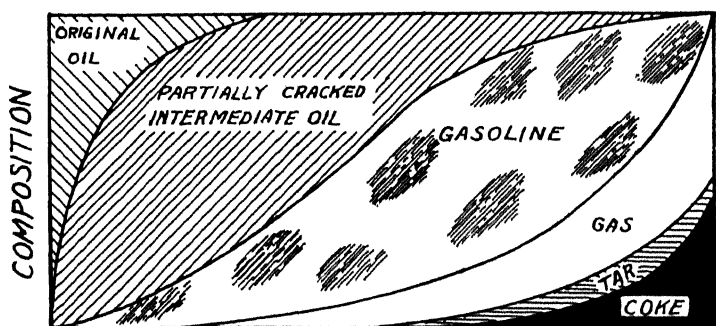
The results of the experiment show that after one hour of cracking at 425°C . only 14.5 per cent of the original product was left. The original fraction, however, was greatly aromatized, its specific gravity being changed from 0.912 to 0.963. All other fractions were newly formed in the process of cracking, including 69.8 per cent of fractions having a

Table 27. Distillation of Products Obtained by Cracking the Lubricating Oil Fraction B.P. 250 to 280°C. at 6 mm.

Pressure (mm.)	Boiling Range of Fraction (°C.)	% Off by Weight	Sp. Gr. at 15°C.
	Gases	6.7	
Atmospheric	Below 200	22.4	0.735
"	200-300	18.9	0.851
5	145-200	7.4	0.908
5	200-250	14.4	0.945
5	250-285	14.5	0.963 (Initial Boiling Range)
5	285-346	6.1	0.989
	Residue	4.0	
	Loss	5.6	

lower molecular weight than the original product, and 10.1 per cent of heavier fractions.

In the initial stages of cracking of heavy oils, fractions distilling in the boiling range of gas oils and kerosenes are predominantly formed. The yield of gasoline gradually increases with increasing time of cracking. The formation of high-boiling cracked fractions at the beginning of cracking is due to the decomposition of more unstable high molecular weight hydrocarbons (Chapter 1). Gasoline and gas are readily formed in the



PROGRESSION THROUGH CRACKING COIL

Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 4.—Composition of Synthetic Crude versus Time of Cracking.

further stage of cracking, as a result of the decomposition of more stable hydrocarbons of lower molecular weight, as well as of intermediate fractions formed in the first stage of the process.

The whole picture of cracking versus time may clearly be illustrated by the scheme of Strout⁴³ given in Figure 4.

The cracking of high-boiling residues and asphalts may form heavy hydrocarbons of lubricating oils in the initial stages. Nelson and Fancher³⁴ cracked heavy residues under mild conditions of distillation to coke. The process was carried out under the low pressure of 14 mm. or less. The lower the pressure, the shorter was the time of cracking. The viscosity of the resulting decomposition products depended upon the

pressure or the time of the process. A Pennsylvania bright stock of A.P.I. gravity 28, Saybolt viscosity 80 at 210°F., was distilled to coke at 14 mm. pressure. As a result 90 per cent of neutrals of A.P.I. gravity 30 and Saybolt viscosity 208 at 100°F. were formed. The destructive distillation of an asphalt to coke gave the following results depending upon the pressure (Table 28).

Table 28. Decomposition of Asphalt at Different Pressures.

Pressure (mm.)	Yield of Liquid Products	Kind of Product	Properties of Products
18	72	Cylinder stock	Visc. 93 sec. at 210°F.
22	69	Heavy neutral	" 600 sec. at 100°F
380	65	Distillate	Grav. 35 A.P.I.
450	63	Kerosene	E.P. 560°F.
150 lbs./sq. in.	53	Gasoline	

These data clearly show that the average boiling range or molecular weight of cracking products depends upon the time of cracking.

Rate of Cracking

Due to various reactions which take place in cracking the rate of cracking cannot be satisfactorily determined or calculated. Assuming that the formation of gas, gasoline and other decomposition products is a monomolecular reaction, the following well-known equation for constant temperature may be applied to the rate of cracking:

$$-\frac{dx}{dt} = k(A - x) \quad (32)$$

or after integration

$$k = \frac{1}{t} \log \text{nat} \frac{A}{A - x}, \quad (32a)$$

where k is the reaction velocity constant, t the reaction time, A the initial concentration of the product, and x the amount of the product cracked in time t .

However, this equation may be applied to cracking only on the basis of certain arbitrary assumptions. It is assumed, for instance, that x corresponds to the amount of gas and gasoline formed, and $A - x$ to the amount of residuum or recycle stock. Such assumptions are evidently very approximate, because the gas and gasoline are only a part of the decomposition products, and also because the residuum or recycle stock consists largely of the condensation and aromatization products formed in cracking. The equation may be applied with more exactitude to the first stages of cracking, when the extent of condensation processes is comparatively small.

The experiments of Geniesse and Reuter,¹⁴ Keith, Ward and Rubin²⁶ and others show that equation (32), for the monomolecular reactions, is approximately valid for the formation of gas and gasoline, or gasoline.

The velocity-constants of cracking, k , are independent of pressure, as can be expected for monomolecular reactions.

Cracking begins as soon as the temperature is sufficiently high. There is no induction period during which the formation of cracking products does not take place to any appreciable extent.

The rate of cracking at a constant temperature is approximately proportional to the time at the beginning of the process, as should be expected from equation (32). Usually the linear relationship between the yield of gasoline and time is valid up to 15-20 per cent of gasoline formed. The data in Table 29 illustrate the rate of gasoline formation in cracking.

Table 29. Formation of Gasoline in Pressure Cracking of Light Straight Run Gas Oil at 425°C. (797°F.)

Time of Cracking (min.)	Yield (% by Volume)
15	5
30	10
60	20
90	26
120	30
240	44
360	47
480	42

The percentage of cracked gasoline, increasing with time of cracking, reaches its maximum and then gradually decreases at the expense of the formation of coke and gas, as will be seen from Figure 4. The maximum yield of gasoline in a once-through operation depends upon the nature of the cracking stock. For gas oils, it is approximately from 45 to 50 per cent by volume. The time required to obtain the maximum yield depends upon the temperature, being about 5 hours for cracking gas oils at 425°C. (797°F.).

The rate of formation of all other liquid cracked products follows the same regularity. In the case of cracked kerosene fraction, boiling in the range of 200-300°C. (392-572°F.), the rate of formation exceeds that of cracked gasoline in the first stages of cracking, reaches its maximum and decreases earlier as compared with cracked gasoline. It should be remembered that the low molecular weight cracked fractions are thermally more stable than those of high molecular weight. Thus, the formation of gasoline proceeds at the expense of high-boiling cracked fractions formed in the earlier stages of cracking.

The maximum yield of cracked gasoline in a once-through operation is much smaller in vapor-phase cracking at high temperatures. Under these rather severe conditions, the secondary decomposition reactions of gasoline formed interfere with the primary reactions in the first stages of the process, resulting in high yields of gas and in a decrease of gasoline yields. Some selected data of Geniesse and Reuter¹⁴ are given in Table 30.

Thus, in vapor-phase cracking at 600°C. the maximum yield of cracked gasoline per pass does not exceed 23-24 per cent. As can be seen

Table 30. Formation of Gas and Gasoline in Vapor-Phase Cracking of Straight-Run Gas Oil at 600°C. (1112°F.) and Atmospheric Pressure.

Time (min.)	Yield of Gasoline (% by Volume)	Yield of Gas (% by Weight)
0.051	13.8	11.5
0.061	17.6	11.7
0.107	20.7	24.2
0.123	23.3	25.8
0.139	23.5	25.7
0.145	23.7	25.2
0.192	22.5	32.2
0.266	23.7	37.6

from the figures of the gas formation, the yields of gas are very high even in the first stage of cracking.

Rate of Cracking for Various Products

Other conditions being equal, the rate of cracking depends upon the boiling range of charging stocks, as well as upon the chemical nature of the latter. Table 31 includes the cracking data of various fractions of the same crude at 425°C. (797°F.) for 1 hour in a once-through operation. The yields of gasoline and those of all newly formed fractions below and above the boiling range of the charging stock are given in the table.

The data of Table 31 show that the rate of cracking is lowest for the lightest fractions and gradually increases with increasing boiling range of the fraction. The total rate of cracking, *i.e.*, the formation of all cracked products, depends more upon the boiling range than does the rate of formation of gasoline.

Table 31. Yields of Cracked Products from Various Stocks in Cracking at 425°C. (797°F.) for 1 Hour.

Cracking Stock	Boiling Range (°C.)	Yield of Gasoline* (% by Wt.)	Yield of All New-Formed Fractions (% by Wt.)
Naphtha	180–220	..	17
Kerosene	220–270	15	25
Gas oil	270–300	16	33
Gas oil	300–325	18	46
Residuum	Above 300	18	..
Heavy Luboil Dist.	250–280 at 6 mm.	22	85

* E.P. 200°C. (392°F.).

Figure 4a represents the cracking rates or constants k of equation 32 versus temperature in °F. for various stocks and hydrocarbons. At the same temperature the cracking rate of butanes is approximately 25 times less than that of gas oil. The cracking rate of low molecular weight paraffins (propane, ethane and methane) decreases sharply with decreasing molecular weight.

In commercial operation the rate of cracking of naphtha or kerosene is appreciably smaller than that of heavy gas oils or residues.

The close relationship between the rate of cracking and the boiling range of petroleum products is explained by the thermal instability of long paraffinic side chains and high molecular weight paraffins which are

largely represented in high-boiling products. The low-boiling products contain comparatively short side chains or low molecular weight paraffins which are thermally more stable (Chapter 1).

At the same boiling range, the rate of cracking depends upon the chemical nature of the charging stock, other conditions being identical. Aromatic charging stocks are more refractory or resistant to cracking, and their cracking rate is lower in comparison with paraffinic charging stocks.

As has been stated in Chapter 1, high molecular weight paraffins, or paraffinic side chains of cyclic hydrocarbons, are decomposed much more easily than naphthenes—particularly aromatics with short side chains. Thus, the rate of cracking is closely connected with the percentage and molecular weight of paraffins and paraffinic side chains in charging stocks.

The straight-run gas oils of the same boiling range, produced from paraffin or asphaltic base crudes, have approximately the same rate of cracking. The difference in the paraffinic side chains of various straight-run products of the same boiling range is too small to effect an appreciable difference in the rates of cracking. On the contrary, the cracked or recycled products have a much lower rate of cracking than the straight-run products. The paraffinic side chains of recycle products are much shorter, and the cyclic hydrocarbons with short side chains are much more resistant to cracking than the hydrocarbons of straight-run products.

The cracking rate of recycle stocks depends upon the aromaticity, or upon the cracking conditions under which a recycle stock is produced. The recycle stocks of high aromaticity or high specific gravity, produced under very severe conditions of cracking, have the slowest rates of cracking. According to Leslie and Potthoff,²⁹ the rate of gasoline formation for a "thermolized" oil of specific gravity 0.931 is from two to three times smaller than that for a straight-run oil of specific gravity 0.850. The data on the rate of cracking of recycle oils after repeated recyclings³⁰ are given in Table 32. The virgin distillate was a gas oil of specific gravity

Table 32. Rate of Gasoline Formation of Straight Run and Recycle Oils.

Times Cracked	Sp. Gr. at 15°C.	Cracking Conditions				Yield (% by Vol.)
		Temp. (°C.)	Temp. (°F.)	Pressure (atm.)	Time (min.)	
First	0.872	452	842	40	60	30
Second	0.886	452	842	40	60	23
Third	0.891	452	842	40	60	14
Fourth	0.939	452	842	40	60	8
Fifth	0.963	452	842	40	60	3
Sixth	0.969	452	842	40	60	2

0.872 (30.8 A.P.I. gravity). The boiling range of all recycle stocks was the same from 200 to 350°C. (392 to 662°F.).

Thus, the rate of gasoline formation gradually falls with increasing aromaticity or specific gravity of recycle oils. The rate of gasoline formation for customary recycle stocks in the mixed-phase process may be assumed to be approximately 2½ times smaller than that for straight-run gas oils.

As has been shown above, the crackability of petroleum products depends upon the boiling range and the chemical composition. Since the aromaticity or paraffinicity of petroleum products is in close correlation with the specific gravities or aniline points, a certain relationship between the crackability and the values of specific gravity or aniline point should be expected.

Watson and Nelson⁵⁶ showed that the characterization factor $K = \frac{\sqrt[3]{T}}{S}$ where T is the molar average boiling point (degrees Rankine) and S the specific gravity at 60/60°F., predetermines the paraffinicity of petroleum products. For the fractions of a paraffinic crude this factor is close to 12.5, for those of Mid-continent crudes it varies from 12.4 to 11.8, and for aromatic or naphthenic stocks it approaches 10 as the minimum value.

The characterization factor, being constant for various fractions of the same crude, cannot be used as the index of crackability of petroleum stocks. A simpler function, $C = \frac{T}{S}$ where T is the average absolute boiling temperature of the product and S the specific gravity at 60/60°F., may be used as an approximate index of crackability (or refractoriness) of various petroleum stocks. Table 33 contains the values of C calculated for fractions of a paraffin base and a naphthenic base crude, as well as for some pure hydrocarbons.

The data of Table 33 show an approximate correlation between the crackability of the stocks and the values of the factor C . It is of interest that the pure hydrocarbons follow the same relationship. The most refractory benzene has the minimum value of C of 405, and the most crackable paraffin base gas oil has the maximum index value of 666.

Table 33. Crackability Index $\frac{T}{S}$ of Various Stocks and Hydrocarbons.

Stock	Average Boiling Point (Abs. Temp.)	Sp. Gr. at 60/60°F.	Index
Gasoline, paraffin base	398	0.730	545
Kerosene, paraffin base	513	0.800	641
Gas Oil, paraffin base	573	0.860	666
Gasoline, naphthenic base	398	0.750	531
Kerosene, naphthenic base	513	0.830	618
Gas Oil, naphthenic base	573	0.900	637
Recycle gas oil	573	0.930	616
Butane	273	0.600	455
Cyclohexane	353	0.770	453
Benzene	353	0.870	405
Methylnaphthalene	576	1.025	504

Rude, Junkins and Barnes^{37a} have found that the yield of gasoline and gas per pass at the same temperature is proportional to the product AG , where A is the aniline point and G the A.P.I. gravity. Both properties depend on the chemical nature of cracking stocks, increasing with increas-

ing paraffinicity. The product AG , however, does not include the boiling temperature of cracking stocks, and the application of this relationship to different fractions of the same crude would give quite erroneous results. Thus the above relation should be applied only to cracking or recycle stocks of the same approximate boiling range.

Rate of Cracking and Temperature

Temperature is the most influential factor in the rate of cracking. The theoretical relationship between the velocity-constant k and the temperature T is given by the Arrhenius equation:

$$\frac{d \log \text{nat } k}{dT} = \frac{Q}{RT^2} \quad (33)$$

or after integration

$$\log \text{nat } k = -\frac{Q}{RT} + C,$$

where k is the reaction-velocity constant, T the absolute temperature, Q the activation energy, R the gas constant, and C the integration constant. This equation may be applied to cracking with the same approximation as equation (32). The values of the activation energy vary in different sets of experiments from 53,400 to 67,200 cal., and those of C from 29 to 33 in the temperature range from 400-600°C. (752-1112°F.). The activation energy depends upon the boiling range and chemical composition of oil products (Obriadchikoff^{35a}). The activation energy decreases with increasing boiling range of the product. At the same molecular weight aromatic products have higher values of activation energy than do paraffinic products. The most probable values of the above-mentioned constants in pressure cracking of gas oils are given by the following equation:

$$\log \text{nat } k = -\frac{60,000}{RT} + 30. \quad (34)$$

The ratio between the velocity-constant K_{T+10} and k_T at the temperatures $T + 10$ and T is usually specified as the temperature coefficient of the rate of cracking (as well as of any other reaction). The following equation for the coefficient $\frac{K_{T+10}}{K_T}$ is obtained on the basis of equation (34):

$$\log \text{nat } \frac{K_{T+10}}{K_T} = \frac{600,000}{2T(T+10)} \quad (35)$$

Equation (35) gives the following figures for the coefficient $\frac{K_{T+10}}{K_T}$ at various temperatures of cracking (Table 34). The temperature dif-

ferences required for doubling the rate of pressure cracking are given in the same table.

Table 34. Temperature Coefficients of the Velocity Constants of Pressure Cracking.

—Cracking Temp.— (°C.) (°F.)		Temperature Coefficient $\frac{K_{T+10}}{K_T}$	Temperature Difference for Which Reaction Rate Doubles In (°C.) (°F.)	
400	752	1.92	11	20
500	932	1.65	14	25.5
600	1112	1.48	17	30.5

The same values of the coefficients may be applied to the formation of gasoline in cracking, if the yield of gasoline does not exceed 20 per cent by volume in a once-through operation. If the yield of gasoline is greater, the data of Table 34 have to be applied to the total formation of gas and gasoline. The gas formation in pressure cracking is not significant up to 15-20 per cent of gasoline formed.

Thus, the rate of cracking is almost doubled for every 10°C., when the temperature of the process is about 400°C. (752°F.), as has been found experimentally by Leslie and Potthoff²⁹ and Sachanen and Tili-cheyev.³⁸ The temperature coefficient of cracking decreases with increasing temperature.

According to Geniesse and Reuter¹⁴ and Schutt,⁴⁰ the coefficients $\frac{K_{T+10}}{K_T}$ are lower for vapor-phase cracking under atmospheric and low pressures. Table 35 includes some data of Schutt on this process. Dintzes and his associates^{5a} give close figures, from 1.38 to 1.48, for the temperature coefficient of vapor-phase cracking of straight-run fractions within the range of 500-600°C. The temperature coefficient of vapor-phase cracking of a cracked gas oil has been determined as 1.66.

Table 35. Temperature Coefficients of the Velocity Constants of Vapor-Phase Cracking.

—Cracking Temp.— (°C.) (°F.)		Temperature Coefficient $\frac{K_{T+10}}{K_T}$	Temperature Difference for Which Reaction Rate Doubles In (°C.) (°F.)	
482	950	1.6	15.5	28
565	1050	1.5	18	33
621	1150	1.4	21	38

A small difference in the coefficients $\frac{K_{T+10}}{K_T}$ of pressure and vapor-phase cracking may be explained by a smaller value of the activation energy in the latter. It is believed, however, that this difference is due to the large extent of secondary decomposition reactions in the vapor-phase process. As a matter of fact, the yields of gas in the experiments of Geniesse and Reuter were very high, for instance, 20-40 per cent by weight corresponding to yields of gasoline of 20-30 per cent by volume. In pressure cracking the yield of gas would be only five per cent under these conditions. The secondary decomposition to gas of a part of the gasoline formed is evident.

Thus, it is probable that the relationship between rate of cracking and temperature is identical for the pressure and vapor-phase processes. The deviations of the latter may be ascribed to the secondary decomposition reactions that occur readily in vapor-phase cracking.

Equation (35) and the data of Table 34 may be used for calculation of the yields of gasoline or gas and gasoline *versus* temperature, if the data of yields at one temperature are available. The most reliable data on the formation of gasoline *versus* time are obtained in bomb operations at moderate temperatures, when the time of cracking is comparatively long. The data pertaining to continuous operation are less reliable due to many more or less arbitrary assumptions involved in the calculations of volumes of products under cracking conditions.

Table 36 includes the data on the formation of cracked gasoline from light gas oils at 425-428°C. (797-800°F.) obtained by Leslie and Potthoff²⁹ and Sachanen and Tilicheyev³⁸ in pressure operation.

Table 36. Yields of Cracked Gasoline in Pressure Cracking from Light Gas Oils.

Gas Oil, Sp. Gr. 0.850 Boiling Range: 213°-392°C. (415°-737°F.)		Gas Oil, Sp. Gr. 0.834 Boiling Range: 270°-300°C. (518°-572°F.)		Gas Oil, Sp. Gr. 0.859 Boiling Range: 300°-325°C. (572°-617°F.)	
427°C. (800°F.)		425°C. (797°F.)		425°C. (797°F.)	
Time (min.)	Yield of Gasoline (% by Vol.)	Time (min.)	Yield of Gasoline (% by Vol.)	Time (min.)	Yield of Gasoline (% by Vol.)
30	10.9	34	10.5	65.5	20.8
60	16.3	64	18.0		
91	21.7	184	28.0*		
134	28.1				

* This yield seems to be too small due to excessive losses.

The accordance between the data of Table 36 is satisfactory, and the following yields of cracked gasoline from light straight-run gas oils at 425°C. (797°F.) may be accepted: 10 per cent for 30 minutes, 20 per cent for 1 hour and 30 per cent for 2 hours. These figures are in accordance with the latest data of Tilicheyev^{46a} on the cracking of high molecular weight paraffins at 425°C. for 60 minutes. The yield of gasoline under these conditions was 17 per cent by weight, or 19.5 per cent by volume. On the basis of the data of Table 34, the yields of cracked gasoline *versus* time have been calculated for various temperatures, and the figures obtained are summarized in Table 37.

Table 37. The Required Duration of Cracking of Light Gas Oils in the Pressure Process.

Temperature °C. °F.			Temperature °C. °F.			Temperature °C. °F.		
Time			Time			Time		
1. To form 10 per cent by volume of gasoline, 400°F. E.P.			2. To form 20 per cent by volume of gasoline, 400°F. E.P.			3. To form 30 per cent by volume of gasoline, 400°F. E.P.		
400	752	150 min.	400	752	5 hrs.	400	752	10 hrs.
425	797	30 "	425	797	60 min.	425	797	2 "
450	842	6 "	450	842	14 "	450	842	28 min.
475	887	90 sec.	475	887	3 "	475	887	6 "
500	932	25 "	500	932	50 sec.	500	932	100 sec.
525	977	7 "	525	977	14 "	525	977	28 "
550	1022	2 "	550	1022	4 "	550	1022	8 "

The cracking durations for the same yields and temperatures calculated from the data of Keith, Ward and Rubin,²⁶ obtained in the continuous process, are approximately 35-40 per cent shorter than those given

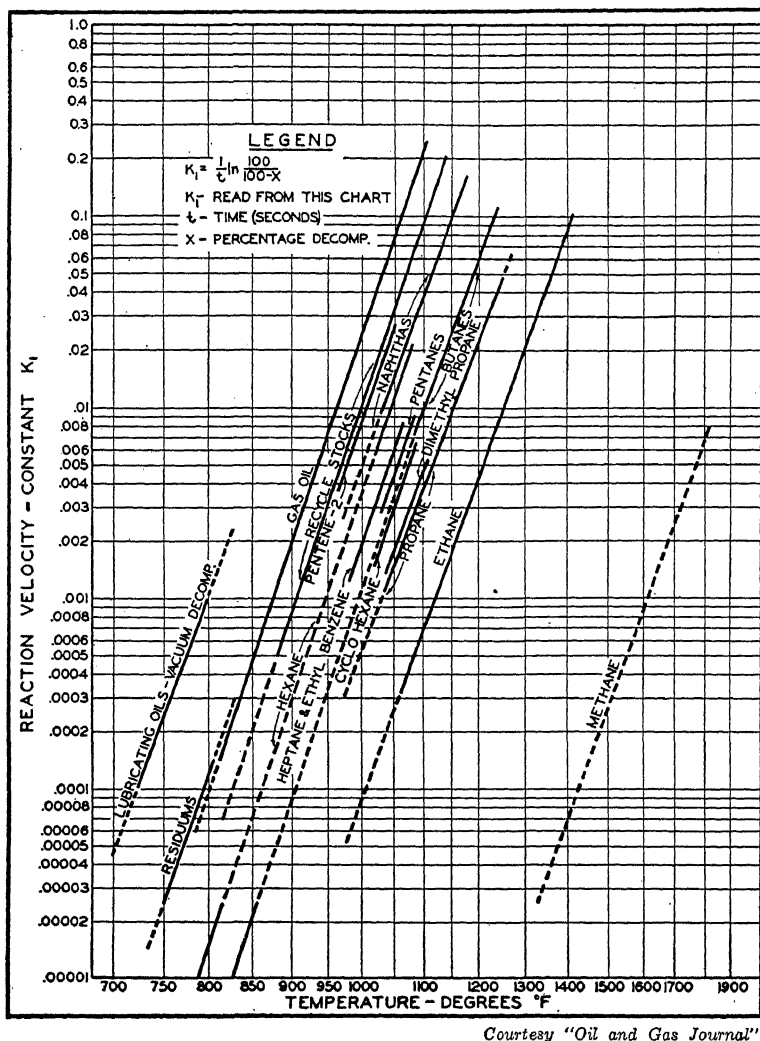


FIGURE 4a.—Cracking Velocity versus Temperature.

in Table 37. The difference may be due partially to the method of calculation of cracking time in the continuous operation and partially to the heavier fractional composition and easier crackability of the gas oil used by the authors cited above. On the contrary, the cracking rates of gas

oil, calculated from the diagram of Nelson,^{33a} are very close to those of Table 37. Figure 4a represents the cracking constants K_1 of various hydrocarbons and oil *versus* temperature in °F. (Nelson). The constant K_1 corresponds to k of equation (32a). The time required for cracking of oils is calculated on the basis of equation (32a) in which A is replaced by 100 and x by the volume per cent of 400°F. gasoline produced by cracking. For individual hydrocarbons, x represents the percentage of mols reacted. The diagram should be used for yields of gasoline and cracked products not exceeding 25 per cent.

At the same yield of gasoline, the time indices of Table 37 are from 20 to 30 per cent shorter when heavier gas oils or residual stocks are cracked. On the other hand, the time indices have to be increased about $2\frac{1}{2}$ times, when cracking recycle oils.

Huntington and Brown²⁴ investigated the cracking of a combined feed containing about 75 per cent of recycle stock. A.P.I. gravity of the feed was 24.8 (sp. gr. 0.905) and the boiling range from 172 to 410°C. (342 to 770°F.). At 422°C. (794°F.) the formation of 9.42 per cent of gasoline required 137.4 minutes and that of 13.35 per cent of gasoline required 167.8 minutes. Comparison of these figures with the data of Table 37 shows that the rate of cracking for recycle oil is approximately 3 to 4 times smaller than in the case of light straight-run gas oils at the same temperature. The data of Table 32 give very close figures for recycle oils of the same specific gravity.

The data of Table 37 pertain to pressure cracking or cracking in mixed-phase. The cracking rate in the vapor-phase process may be calculated on the basis of the data of Geniesse and Reuter.¹⁴ The investigations of these authors give a series of data on the rate of gas and gasoline formation in vapor-phase cracking under atmospheric pressure. As a charging stock, a Mid-continent gas oil was employed. Table 38 contains the data on the yields of cracked gasoline *versus* temperature and time, corresponding to the experiments of the above authors, with minimum gas formation or in not very advanced stages of cracking. The data of Dintzes *et al.*^{5a} on the vapor-phase cracking rate of some Russian gas oils, however, are much lower than those of Geniesse and Reuter (approximately $1/3$ of those calculated from Geniesse and Reuter's data).

Table 38. The Required Duration of Cracking of Light Gas Oil in the Vapor-phase Process.

Temperature °C. °F.			Time	Temperature °C. °F.			Time
1. To form 10 per cent by volume of cracked gas- oline.				2. To form 20 per cent by volume of cracked gas- oline.			
500	932		50 sec.	500	932		5 min.
550	1022		10 "	550	1022		30 sec.
580	1076		3 "	580	1076		10 "
600	1112		1 "	600	1112		4 "
640	1184	0.5	"	640	1184	1.5	"

It should be emphasized, however, that the data of Table 38 are not comparable to those of Table 37 for pressure cracking due to the gas-forming secondary reactions which take place readily in the vapor-phase process. Thus, gas formation corresponding to the same yields of cracked gasoline is greater in the vapor-phase process than in pressure cracking. As a result, the same yields of cracked gasoline in the vapor-phase and pressure processes correspond to the different total conversions, and are greater in the vapor-phase than in the pressure process.

Comparison of Tables 37 and 38 shows that the times required to form 20 per cent gasoline in the pressure process and 10 per cent gasoline in the vapor-phase process are approximately equal. The gas formation in the first case is only 1 per cent (Table 47), while in the second case it amounts to 10 per cent (Table 30). Thus, the total yields of gas and gasoline in the pressure process, forming 20 per cent gasoline, and in vapor-phase cracking, forming 10 per cent gasoline, are approximately equal.

Rate of Cracking and Pressure

The influence of pressure upon the rate of cracking is a most disputed question. From the theoretical standpoint, the velocity constant of monomolecular cracking reactions should be independent of the pressure. However, the secondary bi- and polymolecular reactions of cracking, such as polymerization and condensation, should be affected by pressure, as will be seen later. A little has been done on the kinetics of decomposition of pure chemical compounds in the liquid phase under high pressures. Williams, Perrin and Gibson^{56b} investigated the decomposition of phenylbenzyl-methyl-allyl ammonium bromide in chloroform solution under pressures of 1 to 3000 kg./cm.² The influence of pressure was negligible. The reaction was slightly retarded by pressure. It was believed that the pressure was one of the most important factors in cracking, strongly affecting the yields of cracked gasoline. Leslie and Potthoff²⁹ were the first to study the effect of the pressure upon the kinetics of gasoline formation in cracking. The pressure of the added nitrogen had no effect on the cracking. In other experiments the pressure was built up by the decomposing oil from 200 to 500 pounds per square inch gauge at 800°F. Practically no effect of pressure on the yields of gasoline was observed.

Sachanen and Tilicheyev³⁹ investigated the cracking of some fuel oils under various pressures. The results are given in Table 39.

The data of Table 39 show clearly that the pressure has no appreciable effect on the yields of cracked products, *i.e.*, gasoline and kerosene.

The data of Keith, Ward and Rubin²⁶ on cracking of a gas oil under the pressures of 100 to 750 per square inch gauge do not show any considerable influence of the pressure on the yields of gasoline. There is, however, some slight tendency toward higher rates of cracking at higher pressures, as may be seen from Figure 2 of the original article.

Sydnor⁴⁵ studied the effect of the pressure on the ultimate yields of

Table 39. Cracking of Fuel Oils Under Various Pressures at 425°C. (797°F.).

Yields by weight on Char					Kerosene, Boiling Range 200-300°C. (392-572°F.)
Time (min.)	Pressure (atm.)	Gas + Loss	Gasoline, E.P. 200°C. (392°F.)		
Grozny Mixed Base Fuel Oil, Sp. Gr. 0.906					
33	10	2.7	9.8		15.2
33	20	4.9	9.7		14.1
33	30	6.1	9.8		14.3
33	40	7.6	9.9		15.3
Surachany Paraffin Base Fuel Oil, Sp. Gr. 0.8					
94	20	6.5	21.6		22.1
94	40	8.5	19.5		20.4
90	80	6.2	20.4		18.2

gasoline from a Mid-continent gas-oil in a recycle operation. He found that the yields depend to a certain extent on the pressure, decreasing with increasing pressure, as can be seen from Table 40.

Table 40. Ultimate Yields Secured by Cracking a 33.7° A.P.I. Gas Oil.

Pressures (lbs./sq. in.)	200	750	200	750	200	750
Temperature (Soaker) (°F.)	860	860	900	900	900	900
Conversion per pass (%)	7.5	7.5	7.5	7.5	20	20
Yield of gasoline corrected to coke-free basis (% by vol.)	67.4	63.0	66.8	61.5	60.2	57.2
Residuum 12° A.P.I. (% by vol.)	28.1	30.0	27.5	29.6	27.5	33.6
Gas (% by weight)	10.2	11.4	11.3	12.6	16.9	12.2

The recycle operation, used in Sydnor's experiments, may explain the results obtained. All data on the effect of pressure previously mentioned were obtained in a once-through operation and at low yields of gasoline not exceeding 20-25 per cent. Very high yields of gasoline, up to 65 per cent in the experiments of Sydnor, are a result of the recycle operation and of long total cracking time, which favors condensation and polymerization reactions. The decrease in the ultimate yields of gasoline under high pressures is evidently due to the partial condensation of unsaturates, boiling in the boiling range of gasoline, to high-boiling products. It should be emphasized, however, that the decrease in the gasoline yields is not great, not exceeding 3 to 5 per cent on the charge or 5 to 8 per cent on the gasoline, when the pressure is increased from 200 to 750 pounds per square inch gauge.

A comparatively small but appreciable influence of the pressure on the gasoline yields was observed by Huntington and Brown²⁴ for a recycle stock of 24.8 A.P.I. gravity. The experiments at 450°C. (844°F.) under pressures of 300 to 900 pounds per square inch gauge for 40 minutes showed the increase in gasoline yield to be from 15 to 20 per cent.

Nametkin and Gerassimov³² applied very high pressures to the cracking of a kerosene distillate, varying from 994 to 6,035 pounds per square inch gauge. The rate of cracking was not affected by the variations in the pressure, and the yields of the fractions boiling below 150°C. and those boiling between 150 and 200°C. were unchanged.

The following conclusions may be drawn from the investigations discussed above. The pressure does not appreciably affect the rate of crack-

ing and the rate of formation of gasoline, when the yields of gasoline are not very high. In the recycling operation the yields of gasoline under high pressures may be somewhat lower than under low pressures due to the partial condensation of olefins to high-boiling products.

These conclusions seem to be in a certain contradiction with the known and theoretically expected effect of pressure on alkylation, polymerization and hydrogenation reactions described in Chapters 1 and 3. It should be kept in mind, however, that the positive effect of pressure on all these reactions is observed under special conditions which do not exist in conventional cracking. For instance, hydrogenation of aromatics takes place under very high hydrogen pressures and in the presence of specific catalysts. Alkylation of paraffins with olefins occurs in the presence of a great excess of the paraffin under very high pressures. Only polymerization of olefins and some condensation reactions of olefins and aromatics may occur under high-pressure cracking conditions, resulting in a decrease of gasoline yields, as has been mentioned above.

Although the part played by pressure on cracking is of secondary importance, it should not be underestimated. Cracking under pressure assures the most favorable conditions for heat transfer and elimination of local overheating and, therefore, gives little tar and coke. The process under pressure is performed with maximum efficiency and with minimum fuel consumption.

All the conclusions given above are valid for pressure cracking at comparatively moderate temperatures when the yields of gas are relatively small. Even in the recycle operation, the yields of gas usually do not exceed 10 per cent by weight. In the vapor-phase process at high temperatures and low pressures, the rate of cracking and particularly the yields of gasoline are greatly affected by the pressure. Gas formation in vapor-phase cracking is large, and the cracked gas contains a large proportion of olefins and other unsaturates which are polymerized under high pressures, increasing the yield of gasoline. According to Dean and Jacobs,⁴ for instance, the yield of gasoline at a constant rate of feed was almost doubled by increasing the pressure from atmospheric to 200 pounds per square inch gauge.

Effect of Pressure on Secondary Cracking Reactions

As Leslie and Potthoff²⁹ showed, the pressure does not affect the fractional composition of cracked gasolines. The same conclusion can be obtained from the extensive investigations of Keith, Ward and Rubin.²⁸ Cracked gasolines, produced under pressures from 100 to 1000 pounds per square inch gauge with approximately identical extent of cracking, have the same fractional composition independently of the pressure.

This proves once more that the primary cracking reactions of decomposition, leading to the formation of low molecular weight hydrocarbons, are independent of the pressure, as might be predicted for monomolecular reactions. On the contrary, the secondary reactions of polymerization

Table 41. Iodine Numbers and Aniline Points of Cracked Gasoline and Kerosene Obtained at Various Pressures.

Exp. No.	Orig. Crude Oil Product	Cracking Conditions			Cracked Gasoline			Cracked Kerosene Sp. Gr. at 15°C. of Fraction	Cracked and Treated Gasoline		Cracked and Treated Kerosene, 200°-300°C. Fraction	
		Temp. (°C.)	Pressure (atm.)	Duration (min.)	Sp. Gr. at 15°C.	Iodine No.	Aniline Point (°C.)		Sp. Gr. at 15°C.	Aniline Point (°C.)	Sp. Gr. at 15°C.	Aniline Point (°C.)
1	Surachany Fuel Oil	425	10	98	0.736	126.5	44.7	0.839	0.725	67.1	0.802	71.3
2	Surachany Fuel Oil	425	20	94	0.738	89.4	46.8	0.839	0.722	65.0	—	—
3	Surachany Fuel Oil	425	40	94	0.731	70.7	51.2	0.839	0.719	65.2	0.814	69.3
4	Surachany Fuel Oil	425	80	90	0.732	64.3	51.1	0.838	0.717	65.5	—	—
5	Baku Heavy Gas Oil	450	10	48	0.747	144.9	37.1	0.866	0.727	65.4	0.834	66.1
6	Baku Heavy Gas Oil	450	20	51	0.741	131.0	40.3	0.864	0.723	65.3	—	—
7	Baku Heavy Gas Oil	450	40	52	0.748	83.6	41.2	0.878	0.729	61.9	0.847	62.8
8	Baku Heavy Gas Oil	450	100	59	0.766	51.2	33.4	0.929	0.733	59.9	—	—
9	Paraffin Wax	450	10	64	0.717	129.0	49.2	0.784	0.710	70.5	0.775	83.9
10	Paraffin Wax	450	20	64	0.718	110.9	50.6	0.791	—	—	—	—
11	Paraffin Wax	450	30	65	0.709	100.4	50.5	0.793	—	—	—	—
12	Paraffin Wax	450	30	65	0.717	93.1	51.1	0.799	—	—	—	—
13	Paraffin Wax	450	40	63	0.715	79.7	52.1	0.800	—	—	—	—
14	Paraffin Wax	450	100	40	0.716	63.6	55.7	0.810	—	—	—	—
15	Paraffin Wax	450	100	81	0.728	—	50.4	0.836	0.709	63.0	0.813	67.5

and condensation are strongly affected by pressure. Thus, the chemical composition of cracked gasolines, as well as of other cracked products, depends largely on the pressure. Table 41 contains the data of Sachanen and Tilicheyev³⁹ on the iodine numbers and aniline point of cracked gasolines and kerosenes, obtained under varied pressures. The aniline points and specific gravities of gasolines and kerosenes were determined before and after treatment with 3 volumes of sulphuric acid and redistillation, in order to remove unsaturated and aromatic hydrocarbons.

The iodine numbers of cracked gasolines decrease rapidly with increasing pressure. Thus, the cracked gasoline from a Baku heavy gas oil, obtained at a pressure of 100 atmospheres, has an iodine number and a content of unsaturates about three times smaller than that found at 10 atmospheres' pressure. The decrease in the amount of unsaturates is evidently due to their polymerization and condensation under high cracking pressure.

On the other hand, the increase in specific gravity and the decrease in aniline point of cracked gasolines and kerosenes with increased pressure, particularly after treatment with sulphuric acid, show that the percentage of naphthenes becomes greater under high pressures. Thus, high pressures favor the transformation of olefins into naphthenes by isomerization or by any other cyclization reactions. Experiments 9 and 15 of Table 41, pertaining to cracking paraffin wax at 10 and 100 atmospheres' pressure, are of particular interest. On the basis of aniline points after the removal of unsaturates with sulphuric acid, it might be said that the cracked kerosene from experiment 15 (100 atm. pressure) is composed mostly of naphthenes only after the aromatic and unsaturated hydrocarbons have been removed, whereas a similar kerosene from experiment 9 (10 atm. pressure) consists almost exclusively of paraffins. From this example it is clear that the amount of naphthenes in cracked products can be controlled to a great extent by varying the pressure.

The chemical composition of cracked gases also depends upon the pressure of the process. The higher the pressure, the poorer in olefins is the cracked gas. It is well known that the cracked gases obtained in the high pressure cracking process are poor in olefins and rich in paraffins. On the contrary, the cracked gases of the low-pressure vapor-phase cracking, are highly olefinic (Chapter 7). The gaseous olefins produced in cracking are polymerized or condensed in the high-pressure process and remain intact under low pressures.

Pearce and Newsome^{36b} found that cracking hexane at temperatures of 430-520°C. and under pressures of 14,000-15,000 lbs./sq. inch produces cracked gases containing only an insignificant quantity of olefins. The content of unsaturates in liquid decomposition products also was very small under these conditions.

It should be emphasized, however, that high pressure is only one of the factors favoring the secondary reactions of polymerization and condensation. High temperature and long cracking time have the same effect on

the secondary reactions. Waterman and Perquin⁵⁴ showed that the bromine number of cracked gasolines and kerosenes produced in the high-pressure process rapidly decrease with increasing time of cracking at 450°C.

The influence of the time-temperature factor on the aniline points and iodine numbers of vapor-cracked gasolines was studied by Geniesse and Reuter.¹⁴ They used the high-temperature index combining time and temperature into a single function

$$2^{\frac{T-480}{17}} / \text{Time},$$

where the temperature 480°C. has been taken as standard and 17°C. as an increase in temperature approximately halving the cracking time of the vapor-phase process. The aromatization of cracked gasolines computed by aniline points increases with increasing time-temperature index. The content of unsaturates, computed by iodine numbers, first increases with increasing time-temperature index and then gradually decreases, due to the secondary reactions involving unsaturated hydrocarbons formed and their partial condensation to other hydrocarbons.

Thermal Effect of Cracking

The thermal effect of various decomposition reactions of paraffins, as well as of paraffinic side chains varies between -100 and -400 cal. per kilogram, depending upon the molecular weight of the hydrocarbons. The thermal effect of dehydrogenation reactions is greater, being close to -400 cal. The predominancy of the decomposition reactions in cracking, however, should be kept in mind.

These figures, calculated for room temperature on the basis of combustion data, should be more negative at the temperatures of cracking. It is believed, however, that the change in the aforementioned values from room temperature to the average cracking temperature, 500°C., is not very significant and does not exceed 10 per cent. Thus, the thermal effect of cracking should be close to 200-300 cal. per kilogram of all cracked products formed. The thermal effect of cracking is usually calculated per kilogram of cracked gasoline formed. Assuming that the yield of cracked gasoline is about half of all cracked products formed in a once-through process, the magnitude of the thermal effect of cracking should be approximately 400-600 cal. per kilogram of cracked gasoline.

Obriadchikoff³⁵ has made very extensive calculations to determine the thermal effect of cracking based on the experiments of Sachanen and Tilicheyev. The calculations were made according to the equation

$$Q = Q_1 - Q_2,$$

where Q is the thermal effect of cracking, and Q_1 and Q_2 are the total heats of combustion of the original and final products of cracking. The heat of combustion of the components was calculated by their specific

gravities; the heat of combustion of gases was accepted as 11,400 cal., and the combustion heat of pure carbon was taken for coke. The following conclusions are made on the basis of these calculations:

1. The heat of cracking depends largely on the yield of cracked gasoline. The relation of the average values of the thermal effect of cracking to the yield of cracked gasoline per kilogram of gasoline is given in Table 42.

Table 42. Relation of the Thermal Effect of Cracking to the Yield of Cracked Gasoline.

Yield of Cracked Gasoline (%)	Q in Calorie-Kilograms
5	-1000
10	-700
15	-500
20	-380
25	-300
30	-200

The reason for this phenomenon, which appears strange at first glance, is quite clear if the mechanism of cracking is taken into consideration. In the first stages of cracking fractions heavier than gasoline are mostly formed. The gasoline yield is small in these initial stages. The input of heat necessary for the formation of all new-formed fractions, but converted to a small yield of gasoline, will give a very high value of thermal effect in this stage.

2. The heat reaction of cracking depends upon the character of the charging stock. The heat effect per kilogram of cracked gasoline, where the yield of the latter amounts to 20 to 25 per cent, will be -350 calories for light gas oil, -450 to -500 calories for paraffin distillate (heavy gas oil) and -700 to -800 for straight-run residue of 0.905 specific gravity. Evidently, this phenomenon is due to the fact that the formation of cracked gasoline from heavy molecules requires a more severe disintegration and, therefore, a higher input of heat.

Moreover, dehydrogenation reactions readily occur in cracking of heavy oils and absorb an appreciable amount of heat, in addition to decomposition reactions.

3. The heat of cracking depends on the number of recycling operations. Thus, the heat of the cracking reaction for Emba gas oil calculated on one kilogram of gasoline will be as shown in Table 43.

Table 43. Heat of Cracking Reaction for Recycled Emba Gas Oil.

Cracking Operation	Heat of Reaction Cal.
One	-470
Two	-400
Three	-180
Four	+380

Thus, the heat of cracking has maximum negative thermal effect in the first operation, the absolute magnitude of which decreases with the following operations, the value becoming positive in the fourth cracking.

This is due to the exothermic heat effect of the condensation reactions which are more marked in recycling processes than in primary cracking. The condensation reactions are of greater importance in the fourth cracking operation than the decomposition reactions which produce gasoline. This is why the heat effect of the process becomes positive.

Leslie and Potthoff²⁹ determined experimentally the thermal effect of cracking for the catalytic cracking of paraffin wax in the presence of aluminum chloride. They found the values to be from 550 to 1000 cal. per kilogram of gasoline formed.

Weir and Eaton^{56a} published the results of their extensive investigation of the heat of cracking of gas oils. The heat of cracking depends upon the depth of cracking (or upon the yield of gas and gasoline) and upon the pressure. The temperature (500-615°C.) is not of primary importance, as should be expected. The heat of cracking decreases with increasing pressure due evidently to the exothermic secondary reactions favored by high pressures. The heat of cracking, corresponding to 20 per cent of the charge cracked to gas and naphtha, varies from 525 B.t.u. to 350 B.t.u. per pound, depending on the pressure, from 10 to 740 pounds respectively.

Computations of the thermal effect of cracking made by Nelson³³ from the heat balance of commercial cracking units give from 290 to 425 cal. per kilo of gasoline or from 520 to 765 B.t.u. per pound.

The value of the thermal effect of cracking of about 250 cal. per kilo of cracked gasoline (450 B.t.u. per pound) should be considered the most probable figure for the commercial pressure process.

Temperatures and Pressures Used in Commercial Cracking

Commercial cracking processes are classified according to the temperature and pressure conditions employed. The temperature range of various commercial cracking processes is comparatively large, from 440 to 700°C. (824 to 1292°F.), including most gas conversion processes. The pressures used in cracking vary from atmospheric to 100 and more atmospheres.

The cracking of liquid products is performed either at comparatively moderate temperatures and high pressures (mixed-phase process) or at high temperatures and low pressures (vapor-phase process). The temperature range of the thermal conversion of gases corresponds to that of vapor-phase cracking, but the pressure used may be either high or low.

The mixed-phase process takes place at temperatures from 440 to 550°C. (824 to 1022°F.) and under pressures from 20 to 100 atmospheres. All petroleum products, distillates and residues, can be processed in mixed-phase cracking. This is the most important and most widely used method of cracking.

In the earlier stage of commercial cracking, the temperature of the process was much lower, around 400-420°C. (754-788°F.). It was believed that the product to be cracked was entirely in the liquid phase

under the comparatively high pressures used. Thus, the process was specified as liquid-phase cracking or, later, as mixed-phase cracking, in contradistinction to the vapor-phase process, which is performed in vapor-phase at high temperatures and low pressures.

The investigation of McKee and Parker³¹ has shown that the critical temperature of gas oils is below 475°C. (887°F.). The critical temperature of petroleum products may be calculated on the basis of the average boiling point in A.S.T.M. distillation according to the equation:

$$t_c = 1.05t_b + 160,$$

where t_c is the critical temperature and t_b the average boiling point of products expressed in °C. If Fahrenheit temperature is used, 286 is substituted for the figure 160. The agreement between the calculated and determined figures for the critical temperature is very satisfactory, and the deviations do not usually exceed 5°C. In Table 44 some data on the critical temperatures of petroleum products are summarized.

Table 44. Critical Temperatures of Petroleum Products.

Product	A.P.I. Gravity	Average Boiling Point (°C.)	Critical Temperature Observed (°C.)
Gasoline	53.9	136	298
Naphtha	48.2	156	348
Kerosene	42.1	232	407
"300" oil	37.0	283	453
Gas oil	38.2	311	478
Gas oil	28.0	266	470
Transformer oil	24.0		463

Gasoline formed in cracking decreases appreciably the critical temperature of gas oils. Thus, the cracking of gas oils under the temperature conditions used in commercial cracking is a vapor- or gas-phase cracking independently of the magnitude of the pressure. When heavier products are cracked, according to McKee and Parker, the high-boiling fractions of the product are in a dissolved state in the uniform phase obtained. It is entirely possible that these high-boiling constituents are also present in the state of an emulsion or as a fog fairly stable under cracking conditions.

In view of the predominantly vapor- or gas-phase character of modern high temperature-pressure cracking, the term "mixed-phase" process seems to be not quite adequate and should be replaced by a more proper specification "pressure cracking."

There is a definite tendency toward higher temperatures in modern pressure or mixed-phase cracking, due to the gain in octane numbers under more severe cracking conditions. The temperature of cracking depends mostly upon the boiling range of the product to be cracked. Temperatures from 500 to 550°C. (932 to 1022°F.) may be used for reforming naphthas and cracking light kerosenes, whereas gas oils are cracked at lower temperatures, from 490 to 530°C. (914 to 986°F.).

Residual oils are cracked at still lower temperatures, from 450 to 500°C. (842 to 932°F.).

As has been previously pointed out, the use of high pressures in mixed-phase cracking secures the most favorable conditions for heat transfer, elimination of local overheating, coke formation, etc. This factor, being of secondary importance, varies widely in various systems of cracking from 20 to 100 atmospheres, without any substantial effect on the yields of gasoline.

The reaction time in the mixed-phase process varies from 10 seconds to 30 minutes, depending on the temperature of the process, the first figure corresponding to the maximum temperature used and *vice versa*. The conditions of temperature and time in the mixed-phase process are rather moderate. As a result, the gas formation and the extent of secondary reactions are limited. Under the high pressures used, the polymerization or condensation of olefins may be noticeable, resulting in moderate percentage of olefins in gas and gasoline.

Vapor-phase cracking is performed at temperatures from 550 to 650°C. (1022 to 1202°F.), the pressure being low, from atmospheric to 3-5 atmospheres. The high temperature of the process assures sufficient heat transfer even under the low pressures used. It is understood that much higher temperature, up to 800°C. (1472°F.) and higher, may be employed in vapor-phase cracking. Commercially, the temperatures above 650°C. (1202°F.) are prohibitive due to coke formation, rapid wear of tubes, etc. The results of vapor-phase cracking at more moderate temperatures up to 650°C. (1202°F.) differ from those at very high temperatures. The process at very high temperatures produces mostly aromatic hydrocarbons.

Only comparatively light distillates can be cracked in the vapor phase. Heavy distillates, as well as residual oils, treated under the high temperature conditions of vapor-phase cracking, form an excessive amount of coke.

A considerable reducing carbon formation in vapor-phase cracking is obtained by the use of steam which is frequently added to the charging stock to be cracked. The mechanism of this action is not clear. According to Groll,¹⁷ by the action of steam the inner surface of the iron tubes used in the process becomes coated with a layer of black iron oxide (Fe_3O_4) preventing coke formation and deposition. No carbon was formed during the cracking, even in the absence of steam in the tubes which were treated with steam before the process. Groll found that the minimum amounts of steam which prevent carbon formation, when a spray oil is to be cracked, depend on the temperature, being 5 per cent or less at 600°C. and 9 per cent at 750°C. (percentage of liquid water with regard to the total liquid charge of oil and water).

The cracking time in vapor-phase cracking is from 1 to 10 seconds. Nevertheless, the temperature-time conditions are much more severe than

in the case of the mixed-phase process. As a result, the primary decomposition products are subjected to further decomposition, forming considerable quantities of low molecular gaseous products. Therefore, the ratio between the yield of gas to that of gasoline is higher than in the mixed-phase process. An extensive occurrence of condensation reactions which form coke is avoided by proper control of the boiling range of the distillates to be cracked and by moderate conversion per pass. Due to the predominance of decomposition reactions which form olefins, which are not polymerized under low pressures, the gas and gasoline are rich in olefins and other unsaturates.

The data of Groll¹⁷ on the vapor-phase cracking of a spray oil of specific gravity 0.835 (boiling range from 277 to 365°F.) may be illustrative for the process in question. Table 45 gives the data on the formation of gasoline and gas *versus* temperature, reaction time being equal in all experiments.

Table 45. Vapor-phase Cracking of Spray Oil at Atmospheric Pressure.

Temperature (°C.)	600	650	700	750	800	850
	Yields, % by Weight					
Gasoline	17.0	24.5	24.0	19.5	20.0	17.9
Residuum	68.8	30.3	22.8	21.7	22.0	19.1
Gas	14.2	45.2	52.2	58.5	58.0	52.9

The properties of gasoline and gas change very largely with temperature. Gasoline at 600°C. contains a large proportion of olefins, whereas that at 850°C. consists predominantly of aromatic hydrocarbons. The relative amount of hydrogen and methane increases with increasing temperature and that of olefins decreases. A large formation of gas and coke at 850°C., as well as a large proportion of hydrogen and methane in the gas, are significant; they show that only elements and low molecular weight paraffins are stable under extreme temperature conditions.

The temperature-pressure conditions of cracking or thermal conversion of gases differ to a certain extent from those of cracking liquid petroleum products. The temperature of thermal conversion of gases is high, being close to that of vapor-phase cracking, from 500 to 700°C. (932 to 1292°F.). The high temperature used in thermal conversion of gases corresponds to the high thermal stability of gaseous paraffins. On the other hand, high pressures, from 800 to 2500 pounds per square inch, are employed to ensure polymerization of olefins under the thermal conditions of the process. Under low pressures and high temperatures, the thermal conversion of gases yields mostly aromatic hydrocarbons. Thus, the temperature and pressure range of thermal conversion of gases is broader than in both methods of cracking liquid petroleum products. The time of reaction in the thermal conversion of gases varies from 1 second to a few minutes, depending on the temperature.

The temperature-pressure-time conditions of the various thermal cracking processes are summarized in Table 46.

Table 46. Temperature, Pressure and Time in Various Cracking Processes.

	Mixed-Phase Cracking of Liquid Products	Vapor-Phase Cracking of Liquid Products	Thermal Conversion of Gases
Temperature (°C.)	450-550	550-650	500-700
" (°F.)	852-1022	1022-1202	932-1292
Pressure (lbs./sq. in.)	300-1500	15-100	100-2500
Time	10 sec.-30 min.	1-10 sec.	1 sec.-3 min.

Gas Formation in Cracking

Cracked gas, like gasoline, is a decomposition product of cracking. The formation of gas progresses more and more with the duration of cracking at the expense of all other products, due to the greater thermal stability of hydrocarbon gases. As will be seen later, the formation of coke follows the same rule, increasing constantly with the time of cracking. From the thermodynamic standpoint, cracked gasoline and other liquid products of cracking are only intermediates convertible into gases and coke under the cracking conditions. In the final stage of cracking, the charging stock should be entirely converted into hydrogen and carbon which possess a minimum value of free energy. In reality, cracking gases consist of low molecular weight hydrocarbons, including methane, ethane, propane, butanes, ethene, propene and butenes, which are fairly stable under cracking conditions. As has been mentioned in the previous section, hydrogen and methane become predominant when the cracking conditions are very drastic.

The kinetics of gas formation on cracking may be illustrated by the following data pertaining to the high-pressure cracking of a gas oil at 425°C. (797°F.) and given in Table 47.

Table 47. Gas Formation on Cracking Gas Oil at 425°C. (797°F.)

Duration (min.)	Gas, (% by weight)	Duration (min.)	Gas, (% by weight)
30	1	180	6
60	2	240	10
120	4	360	22

Comparison of Tables 29 and 47 clearly shows the difference between the formation of gasoline and of gas in cracking.

There is a very close relationship between the yields of gas and of gasoline in cracking. Keith, Ward and Rubin²⁶ give the following relationships per pass in pressure cracking:

$$1. G = bN + 0.180N^2$$

$$\log_{10} b = \frac{115}{P} - 0.0765$$

for pressure of 100 to 400 pounds gauge inclusive and

$$2. G = 2.32N + 0.0985N^2$$

for pressures of 500 to 1000 pounds gauge. In these equations G is the number of cubic feet of dry gas per barrel of gas oil, N is the percentage of gasoline per pass by volume, and P the pressure in pounds per square inch gauge.

In recycle mixed phase cracking, the ratio between the yields of gas and of gasoline in per cent by volume is close to 1:6, when the commercial yields of gasoline from 50 to 65 per cent are obtained. The ratio is lower for lower yields of gasoline, corresponding to the small yields of gas in less advanced stages of cracking. In vapor-phase cracking the ratio of gas to gasoline is greater, and is close to 1:2 or 1:3 when high yields of gasoline are obtained. Thus, according to DeFlorez,⁵ when Pennsylvania gas oil (40°A.P.I. gravity) was cracked in the vapor-phase at 80 pounds pressure, 61.4 per cent of gasolines and 29.2 per cent of gas were produced, whereas California gas oil (32°A.P.I. gravity) produced 53.89 per cent of gasoline and 26.97 per cent of gas, *i.e.*, the ratio is very close to 1:2. The above yields are given in per cents by volume.

Decomposition of Cracked Gasoline in Cracking

The gasoline formed during the process of cracking is further decomposed to gas and condensed to condensation products, being subjected to the cracking conditions in soaking tubes and reaction chambers. The extent of this decomposition may be computed in the following manner. Special experiments of the author on the cracking of a cracked naphtha showed that about 3 per cent of the naphtha is converted into gas and condensation products when cracked at 425°C. (797°F.) for 1 hour. It is understood that the 3 per cent of gas and condensation products formed does not represent the total conversion of cracked naphtha under the conditions given above. The total amount of cracked products is much higher, but the greater part of the decomposition products boils in the boiling range of gasoline and does not decrease the yield of gasoline.

In Tables 48 and 49 the data on the time required for the formation of various percentages of cracked gasoline at 425°C. are summarized, together with the calculated amounts of decomposed gasoline. For instance, 20 per cent of the theoretical yield of gasoline corresponds approxi-

Table 48. Time Required for the Formation of Cracked Gasoline at 425°C. (797°F.)

Yield of Gasoline (%)	Time (hours)
10	0.5
20	1.0
30	2.0
40	5.0*
50	10.0*

* These figures are very approximate.

Table 49. Formation and Decomposition of Gasoline in Cracking.

Theoretical Yield of Gasoline	-Per Cent of Original Stock- Amount of Decomposed Gasoline	Actual Yield of Gasoline
10	0.08	9.9
20.	0.3	19.7
30	1.0	29.0
40	3.0	37.0
50	7.5	42.5

mately to 10 per cent of the average percentage of gasoline during 1 hour of cracking at 425°C. Under these conditions of temperature and time, 3 per cent of this average percentage, or 0.3 per cent, will be decomposed, resulting in decreasing the actual yield to 19.7 per cent. It has been assumed that the rate of decomposition, 3 per cent per hour, does not depend on the time.

The loss due to the decomposition of cracked gasoline formed in a once-through operation is insignificant at low and moderate yields of gasoline up to 20 per cent. Higher losses accompany high yields of cracked gasoline, amounting to 1 per cent at a yield of 30 per cent, 3 per cent at 40 per cent and 7.5 at 50 per cent, calculated on the charging stock. In the last case, only 42.5 per cent instead of 50 per cent is actually formed. This yield of gasoline is close to the maximum yield in a once-through operation. In the further stages of cracking the yield of gasoline will remain approximately constant for a certain period of time and it will then gradually decrease due to the further decomposition of gasoline. These conclusions are in fair agreement with the previous data on the maximum yield of cracked gasoline in a once-through operation, which has been found equal to 47 per cent (Table 29).

Thus, the yield of cracked gasoline per pass, or in a once-through operation, should not exceed 25 or 30 per cent in order to prevent excessive losses owing to the decomposition of gasoline formed. As will be shown later, coke formation is another factor limiting the yields of gasoline in a once-through operation. In destructive hydrogenation, however, the decomposition of gasoline is the sole factor limiting the yield per pass, since coke formation is practically eliminated in the presence of hydrogen.

Aromatization and Condensation Reactions in Cracking

As has been repeatedly emphasized in Chapter 1, the hydrocarbons form decomposition and condensation products under cracking conditions. First, aromatics and to some extent olefins are responsible for condensation reactions. Aromatization reactions and reactions of dehydrogenation of naphthenes play a very important part in the condensation processes. These reactions forming aromatics are a preliminary stage for further condensations.

The aromatization of cracking stocks may be illustrated by the data of Table 50. The narrow cuts were cracked at 425°C. (797°F.) for one hour. The specific gravities of basic fractions before and after cracking are given in the table.

These data show clearly that, other conditions being equal, the processes of aromatization are more pronounced in the heavier fractions, being hardly noticeable in the naphtha fraction. The heavy fractions, consisting mostly of polycyclic naphthenes, are much more capable of aromatization than the light fractions, consisting predominantly of more stable monocyclic and bicyclic naphthenes.

Table 50. Aromatization of Cracked Fractions at 425°C. for 1 Hour: Specific Gravities of Narrow Cuts Before and After Cracking.

Fraction	Specific Gravity of Original Fraction before Cracking	Specific Gravity of Cracked Fraction in the Same Boiling Range
Naphtha	0.794	0.797
Kerosene	0.809	0.818
Cracked kerosene	0.826	0.833
Light gas oil	0.833	0.842
Cracked gas oil	0.843	0.850
Heavy gas oil	0.859	0.875
Lubdistillate	0.910	0.963

The aromatization of naphthenes does not change appreciably the boiling range of the initial product. On the contrary, the condensation of aromatics forms products of a higher molecular weight and boiling range as compared with the original hydrocarbons. As has been described in Chapter 1, the condensation products may be obtained either by condensation of aromatics or by condensation of aromatics with unsaturates. The polymerization of unsaturates also produces high-boiling hydrocarbons, but this process is of minor importance in cracking liquid products.

The formation of high-boiling polycyclic and polymerized hydrocarbons takes place simultaneously with the aromatization, or follows it. These reactions are responsible for the formation of cracked residues boiling above the end point of the original cracking stock. The high specific gravities of the cracked residues show that the hydrocarbons of the cracked residues belong mostly to polycyclic aromatic hydrocarbons formed as a result of condensation.

The condensation processes progress gradually in the course of cracking, a phenomenon which is indicated by the continuous increase in specific gravity of the residues after stripping gasoline and recycle stock fractions. The specific gravities of cracked residues formed from a straight-run paraffin base residuum are given in Table 51.

Table 51. Changes in the Specific Gravity of Residues After Various Periods of Cracking of Paraffin Base Straight-Run Residuum at 426°C. (799°F.).

Time (min.)	Sp. Gr. of Residue after Distilling off Fractions below 300°C.	Time (min.)	Sp. Gr. of Residue after Distilling off Fractions Below 300°C.
0	0.890	62	0.923
22	0.903	92	0.932
32	0.906	152	1.070

Coke Formation in Cracking

The condensation reactions are followed by coke formation which starts in more or less advanced stages of cracking according to the nature of the charging stock. Table 52 gives the data on the rate of coke formation when a mixed base fuel oil is subjected to cracking for a prolonged period.

Thus coke formation as well as the gas formation progresses continuously with increasing time of cracking. The influence of the nature of the

Table 52. Coke Formation When Cracking Mixed-Base Fuel Oil (Specific Gravity 0.905) for Various Periods.

Cracking Conditions		Amount of Coke* Formed Calculated on Fuel Oil (%)
Time (min.)	Temp. (°C.)	
10	425	0.00
13	425	0.04
18	425	0.16
23	425	0.34
33	425	0.59
64	425	1.33
94	425	3.37
18 at 450° (108 min. at 425°C.)		5.07
92 at 450° (552 min. at 425°C.)		14.00

* The amount of coke or carboids formed is determined by the treatment of the product with benzene in which the coke is insoluble (Chapter 7).

charging stock on coke formation under the same cracking conditions is well illustrated by the data of Table 53.

Table 53. Amount of Coke Formed When Cracking for 1 Hour at 425°C. (797°F.)

Product Cracked	Sp. Gr.	Amount of Coke Calculated on the Product (%)
Paraffin distillate	0.883	0.00
Surachany fuel oil	0.890	0.24
Grozny mixed-base fuel oil	0.906	0.95
Voznesensky asphalt-base crude oil	0.929	1.05
Bibi-Eibat asphalt-base fuel oil	0.931	1.51
Binagady asphalt-base crude oil	0.922	2.22
Kaluga crude oil	0.957	4.92

It should be mentioned that the charging stocks of Table 53, with an exception of paraffin wax, have about the same boiling range, consisting mostly of heavy distillates and residual oils boiling above 300°C. Thus, the coke formation depends directly upon the specific gravity or aromaticity of charging stocks.

On the other hand, the coke formation of various fractions of the same crude depends upon the boiling range of the fraction, increasing with increasing boiling temperature, as can be seen from the data of Table 54.

Table 54. Coke Formation of Various Fractions of a Naphthenic Crude in Cracking at 425°C. for 1 Hour.

Fraction	Specific Gravity	Coke Formed (% by Weight on Charging Stock)
Gas Oil	0.905	0.00
Light Neutral	0.925	0.03
Heavy Neutral	0.940	0.15

The relation of the coke formation to the temperature and time of cracking is explained by the data of Table 55.

Thus, the rate of coke formation increases about six times with a rise in temperature of 25°C., or two times with a rise of 10°C., *i.e.*, the law relating to the increase in rate of coke formation with increasing tem-

Table 55. Coke Formation in Cracking at Various Temperatures.

Time (min.)	Temp. (°C.)	Coke Calculated on the Product (%)
Grozny mixed-base fuel oil.		
62	425	0.95
10	450	1.05
Kaluga crude oil.		
122	400	0.22
21	425	0.11
Kaluga crude oil.		
242	400	4.23
60	425	4.93

perature is approximately identical with that relating to the decomposition process of cracking at 400°C.

The influence of pressure on coke formation is shown in Table 56.

Table 56. Cracking of Grozny Mixed-Base Fuel Oil at 425°C. and at Various Pressures (Duration 32 min.).

Pressure (atm.)	Coke Calculated on Fuel Oil (%)
10	0.59
20	0.57
30	0.83
40	0.84

Thus, within experimental error, the pressure does not have any appreciable influence on the coke formation within the limits of 10 to 40 atmospheres.

The data of Sydner⁴⁵ on the formation of coke in the recycle process may be summarized as follows (Table 57).

Table 57. Coke Formation in Cracking of M. C. Gas Oil.

Temperature (°F.)	860	900	860	900	900	860	900
Pressure lbs./sq. in.	200	200	750	750	200	750	750
Conversion Per Pass (%)	7.5	7.5	7.5	7.5	20	20	20
Yield of Gasoline (%)	69.3	67.0	63.0	61.5	62.1	59.5	57.9
Coke (%)	2.0	0.2	0.0	0.0	2.0	0.8	0.8

With the exception of the first experiment, the effect of the pressure upon the coke formation is comparatively insignificant. It should also be mentioned that the greater coke formation corresponds to the higher yields of gasoline.

According to the experiments of Huntington and Brown,²⁴ coke formation depends to a certain degree on the pressure, decreasing with increasing pressure. For instance, the coke formation in cracking a recycle stock at 450°C. (844°F.) for 40 minutes decreased from 1.51 per cent to 0.48 per cent when the pressure increased from 300 to 900 pounds per square inch gauge. At 423°C. (794°F.) the effect of the pressure was smaller, and at 479°C. (894°F.) the coke formation was about the same under 300 and 600 pounds' pressure.

It should be emphasized that local overheating, leading to local coke formation in the overheated spot, takes place much more easily under low pressures. Practically it is impossible to separate the effect of local coke formation from that of the "true" or "general" coke formation, which would correspond to the temperature of the body of the product being cracked in tubes or in a bomb. Taking into consideration the small and not very definite effect of the pressure on the coke formation observed in the experiments described above, it is probable that the pressure is of no particular importance in cracking as far as coke formation is concerned, provided that the oil is not locally overheated, as frequently happens at low pressures.

Thus, the effects of temperature and pressure on the formation of gasoline and coke in cracking ordinary stocks are identical. As a consequence, with each petroleum product a certain yield of gasoline corresponds to a certain yield of coke, independently of the cracking temperature and pressure, assuming, of course, that overheating is avoided. It should be understood, however, that the conclusions on the effect of temperature and pressure on coke formation are valid only for pressure cracking of ordinary cracking stocks.

From the theoretical standpoint, a positive effect of the pressure upon the coke formation should be expected, since the condensation reactions leading to coke formation are bi- and polymolecular. The insignificant effect of the pressure observed is probably due to a small percentage of coke-forming constituents in ordinary cracking stocks. When highly aromatic stocks are cracked, the positive effect of the pressure on coke formation can easily be observed. On the other hand, the effect of pressure on coke formation in vapor-phase cracking should be much greater due to a high concentration of unsaturates and aromatics.

Cracking of a vapor-phase-cracked distillate (sp. gr. 0.920, boiling range 272-614°F., solubility in sulphuric acid, 43%) was investigated under various pressures. The results are given in Table 57a.

Table 57a. Cracking of Vapor-phase-cracked Distillate.

Cracking Conditions*	Yield of Products					
	Coke and Gas	Coke	Fraction 212-302°F.		Fraction 302-572°F.	
			Yield	Sp. Gr.	Yield	Sp. Gr.
30 min., 600 lbs.	6	0.5	16.4	0.842	45.0	0.957
30 " 1200 "	7	0.5	17.3	0.841	40.0	0.961
30 " 4700 "	24	3.2	14.6	0.850	28.9	0.976
60 " 700 "	10	0.5	17.1	0.849	38.8	0.966
60 " 1825 "	27	3.3	14.4	0.859	29.0	0.976
90 " 975 "	34	3.0	13.7	0.868	26.9	0.977
90 " 2000 "	41	6.5	12.0	0.865	23.6	0.981

* Temperature 900°F. for all.

Thus coke formation increases considerably under very high pressures of cracking of aromatic stocks, as can be theoretically predicted. It is of interest that the gas formation also increases with increasing pressure or, in other words, the polymerization of gaseous olefins is more than

counterbalanced by the decomposition and condensation processes yielding hydrogen and other gases.

Coke formation depends upon condensation reactions. The condensation of aromatic rings produces polycyclic aromatic hydrocarbons of high molecular weight. The next stage is the formation of highly polycyclic and high molecular weight asphaltenes and similar asphaltic compounds. The asphaltenes are further transformed into carboids or coke, insoluble in benzene and other organic solvents. The connection of coke formation with condensation processes is plainly illustrated in the cracking of spindle and engine lubricating fractions from a naphthenic crude (Table 58).

Table 58. Formation of Coke and Condensation Processes.

—Conditions of Cracking—			Yields by Weight on Original Product			Sp. Gr. of Cracked Residue Boiling Above 300°C.	Coke on Original Product (%)
Temp. (°C.)	Pressure (atm.)	Duration (min.)	Cracked Gasoline (%)	Cracked Kerosene (%)	Cracked Residue Boiling Above 300°C. (%)		
			Spindle Oil of Specific Gravity 0.925				
425	10	30	15.7	13.8	66.4	0.947	0.00
425	10	60	19.4	18.2	56.1	0.975	0.03
425	10	90	30.9	21.9	37.7	1.054	0.43
			Engine Oil of Specific Gravity 0.940				
425	10	31	10.4	13.3	73.8	0.964	0.00
425	10	60	19.5	17.5	54.7	1.004	0.15
425	10	89	31.9	19.9	36.8	1.080	1.35

The data of Table 58 show that coke formation begins when the condensation processes are advanced to a considerable extent, corresponding to high values of specific gravity of cracked residues of 0.975 or more. Coke formation is closely connected with the polycyclic aromatic hydrocarbons formed in cracking and concentrated in cracked residues. The kinetics of coke formation (Table 52), the connection between the specific gravity of straight-run residues and coke formation (Table 53), as well as that between the boiling range of fractions and coke formation (Table 51), may easily be explained from this standpoint.

Investigation of the cracking of a paraffin distillate of specific gravity 0.883, before and after removal of aromatics by treatment with fuming sulphuric acid, indicates clearly the part played by aromatics in the formation of asphaltenes and coke (Table 59).

Table 59. Cracking of Paraffin Distillate at 450°C. for 36 Minutes, Pressure 10 Atmospheres.

Original Product	Sp. Gr. (15°C.) of Residue Boiling Above 300°C.	Yield On Original Asphaltenes (%)	Product Carboids (%)
Grozny paraffin distillate before removal of aromatic hydrocarbons	1.029	1.99	3.49
Same product after removal of aromatic hydrocarbons	0.930	0.08	0.11

There is a significant difference between the results of the two cracking experiments. An extensive asphaltene and coke formation took place in

the first case, accompanied by a marked increase in specific gravity of the residuum. In the second case, after the removal of aromatics, the coke formation was only one-thirty-second of that in the first case. Naphthenic hydrocarbons of the paraffin distillate, left after the removal of aromatics by treatment with sulphuric acid, do not form coke in the first stages of cracking. The coke formation starts only in the advanced stages, when a part of the naphthenes is dehydrogenated to aromatics.

Recracking or Recycling

As has been shown in the previous section, coke formation starts when the condensation processes have proceeded to a certain extent, manifested in the high specific gravity of high-boiling fractions and residue. In this stage of cracking the yield of cracked gasoline depends on the nature of the charging stocks. For straight-run light distillates, the yield of cracked gasoline may be as high as 30 per cent before coke formation begins. Therefore, in this case, the maximum yield of gasoline of about 30 per cent per pass is allowable without any appreciable coke formation. For heavier gas oils and particularly residues, the allowable gasoline yields per pass are correspondingly lower, varying between 20 and 5 per cent, the last figure being related to heavy residues. Thus, only distilled oils may be cracked with high yields of gasoline per pass, amounting to 20 per cent or more, without coke formation.

According to Nelson,³³ there is a close relation between the maximum yields of gasoline in a once-through operation and the allowable crack-per-pass which is approximately half of the maximum yield of gasoline in a once-through operation. Higher yields of cracked gasoline with or without minimum coke formation may be obtained as a result of many repeated cracking operations, in which only distillates are cracked after separating and discarding the residues containing coke-forming condensation products.

Sachanen and Tilicheyev³⁹ performed the following experiments of repeated cracking in bomb operations. A gas oil of specific gravity 0.872 was cracked under the conditions specified in Table 60. After the first operation the synthetic crude was separated into gasoline fraction, recycle fraction boiling between 200 and 350°C., and residuum. Only the fraction 200-350°C. was cracked in the second operation, and so on. The results of six consecutive crackings are given in Table 60. Table 61 gives the yields of cracked products with respect to the original gas oil.

The following conclusions may be made on the basis of these experiments.

The specific gravity and aromaticity of cracked gasoline as well as of other fractions and residues, increase with increase in cracking. The products of the fifth and sixth cracking are predominantly aromatic. As a result of gradual aromatization, the rate of decomposition of the recycle stock decreases in each successive cracking operation. Thus, in the sixth recracking the rate of gasoline formation is 15 times less than

Table 60. Recracking of Gas Oil Temperature 450°C. (842°F.), Pressure 40 Atmospheres.

No. of Times Cracked	Time (min.)	Cracked Products						Liters Gas/kg. Gasoline	Residuum (% by wt.)	Sp. Gr. of Residuum
		Gasoline (% by wt.)	Sp. Gr. of Gasoline	Recycle Stock (% by wt.)	Sp. Gr. of Recycle Stock	Gas Loss (% by wt.)				
First	42	28.7	0.746	48.7	0.886	8.3	182	22.6	0.996	
Second	52	21.3	0.769	59.6	0.891	8.6	256	19.1	1.050	
Third	75	16.3	0.797	67.0	0.939	7.0	333	16.7	1.116	
Fourth	101	12.1	0.833	66.8	0.963	7.9	463	21.1	1.177	
Fifth	101	3.9	0.839	75.0	0.969	7.7	849	21.1	1.157	
Sixth	160	8.0	0.873	58.5	0.982	13.8	1525	33.5	1.243	

Table 61. Yields in Cracked Products After Six Consecutive Cracking Operations.

No. of Times Cracked	Yields by Weight of the Original Gas Oil			
	Gas + Loss	Gasoline up to 200°C. (392°F.)	Recycle Stock 200-350°C. (392-662°F.)	Residuum Boiling Above 350°C. (662°F.)
First	8.3	28.7		
Second	4.2	10.4		
Third	2.0	4.7		
Fourth	1.5	2.4		
Fifth	1.0	0.5		
Sixth	1.3	0.8		
Total Yield	18.3	47.5	5.7	28.5
Total Yield (% by Vol.)	20.4	54.5	5.1	20.0

that of the original gas oil. The straight-run products are cracked at a much higher rate than the cracked ones.

The yield of cracked gas with respect to the charging stock and for the same time of cracking decreases with each successive cracking operation, as is the case in the formation of gasoline. The relative amount of gas with respect to the gasoline formed, however, increases with each consecutive operation.

Sydnor and Patterson⁴⁶ investigated the cracking of the recycle oils produced in successive continuous operations. A straight-run gas oil was used as an initial charging stock. The temperature of the operation was held at 855-860°F. and the release pressure was maintained at 759 pounds per square inch gauge. The summarized results are given in Table 62.

Table 62. Calculated Yields for Each Pass When Cutting 12°A.P.I. Fuel Oil.

Yields on fresh stock	Pass 1	Pass 2	Pass 3	Pass 4
Gasoline 400°F. E.P. (% by vol.)	24.3	19.3	16.7	14.9
Cycle gas oil (% by vol.)	63.0	66.2	65.8	64.2
12°A.P.I. fuel oil (% by vol.)	4.9	7.3	10.3	13.9
Gas (% by weight)	5.5	4.2	4.5	5.5
Coke (% by weight)	0.5	0.3	0.7	1.5
Material balance (% by weight)	96.3	96.4	97.4	99.0
Ratio fuel oil yield to gasoline yield	0.20	0.38	0.62	0.93
Ratio gas yield to gasoline yield	0.23	0.22	0.27	0.37

The aromaticity of the recycle oil increased at each pass. The decrease in gasoline yields and the increase in aromaticity were not so marked as in the experiments of Sachanen and Tilicheyev due to the comparatively mild cracking conditions. The increase in yields of the residuum from 4.9 per cent to 13.9 per cent is very marked, indicating the increase in extent of the condensation processes.

It is interesting to note that the octane numbers of the cracked gasolines produced in the four consecutive passes were approximately equal.

This proves that the cracking conditions for the repeatedly cracked gas oils were too mild to produce an advanced cracking of more stable cyclic hydrocarbons.

Geniesse and Reuter¹⁴ investigated the repeated cracking of recycle stocks in the vapor-phase process at 600°C. for 0.083 minute. Gas and gasoline yields dropped with each consecutive cracking, whereas tar and coke yields rapidly increased. The content of olefins in cracked gases continually decreased and that of hydrogen increased with continuing recycling. Thus, the results of repeated crackings in the vapor-phase process are practically the same as in the pressure operation.

In refinery practice, recycle gas oil usually is combined with fresh stock, and the mixture of recycle and fresh stocks is subjected to the cracking conditions. The ratio between the volume of recycle stock and that of fresh feed in the cracking operation is defined as the "recycle ratio." The values of the recycle ratio in cracking practice vary from 2 to 5 depending on the properties of the fresh stock as well as on the cracking conditions. Higher values of the recycle ratio are used for heavier distillates and residual oils.

The yield of cracked gasoline in a once-through operation or per pass in commercial mixed-phase cracking is about 20 per cent for a cracking feed consisting of fresh and recycle gas oils. In vapor-phase cracking, the yields per pass are low, usually not exceeding 10 per cent. As has been stated above, the yield of cracked gasoline (10 per cent in vapor-phase cracking) does not correspond to the same yield of gasoline in the mixed-phase process due to a much larger gas formation. The total conversions corresponding to 20 per cent of gasoline yield in the mixed-phase operation and to 10 per cent in the vapor-phase operation may be very approximately identical.

The average results of the crack-per-pass in the pressure process are given in Table 63. The percentage of gas and tar rapidly increases with

Table 63. Average Yields of Cracking Products in a Once-Through Operation in Pressure Process for Recycle Oil of 24–25° A.P.I. Gravity.

Products	10 Per Cent Gasoline (% by vol.)	Crack-per-Pass	
		15 Per Cent Gasoline (% by vol.)	20 Per Cent Gasoline (% by vol.)
Gas and loss	1	2	4
Gasoline	10	15	20
Recycle stock	86	78	68
Tar (above E.P. of Recycle)	3	5	8

increasing crack-per-pass. Thus, the maximum yield of gasoline corresponds to the lower crack-per-pass and the higher recycle ratio.

Rude *et al.*^{37a} give the following equation for the yield of 380° E.P. gasoline plus gas per pass:

$$P = \frac{AG}{1000} C t 10^{\frac{T - T_0}{f}}$$

where A and G are the aniline point in °F. and the A.P.I. gravity of the stock respectively, t is the actual reaction time, T the temperature in °F., and C , T_0 , and f the constants (0.92, 850 and 73 respectively). As has been stated above, this equation can be applied only to common recycle stocks of the same boiling range.

The use of too high a recycle ratio as well as too low a crack-per-pass is prohibitive from the commercial standpoint, although the minimum coke formation, maximum yield of gasoline and maximum operation time are secured with a high recycle ratio. On the other hand, the operation with too low a crack-per-pass produces gasoline of comparatively low octane numbers, due to the decrease in octane number with decreasing conversion per pass. According to Nelson,³³ the advantages and disadvantages of increasing the crack-per-pass may be summarized as follows:

1. Lower gasoline yield.
2. Higher octane number.
3. An increased tendency to produce coke.
4. The production of more gas.
5. Increased volatility of the light-end of the gasoline.

It is understood that a high throughput of the fresh feed is obtained with a high conversion per pass and a low recycle ratio. The data on the effect of crack-per-pass on octane numbers are given in Chapter 5.

Selective Cracking and Combination Units

At the risk of repetition, it must be stated that the rate of formation of cracked gasoline, as well as of coke, depends upon the boiling range and the chemical composition of the charging stocks. For the same crude the thermal stability of low-boiling fractions is greater than that of high-boiling ones. On the other hand, the cracking produces aromatized recycle fractions which have a comparatively low rate of cracking, as has been discussed in the previous section.

In conventional cracking, the charging stock frequently consists of various fractions of fresh and recycle stocks distilling in a very large boiling range from 200°C. (392°F.) to 350°C. (662°F.) or to 400°C. (752°F.) if clean or distilled stocks are cracked. The boiling range is still larger if a crude or residuum is processed directly without predistillation. This method of cracking cannot be considered as satisfactory from the standpoint of kinetics. Under average cracking conditions, the low-boiling straight-run and particularly recycle fractions will be quite insufficiently cracked. On the other hand, the cracking of some high-boiling fractions will be excessive, and will be accompanied by appreciable coke formation.

It is evident that the cracking of various fractions of a charging stock under selective conditions of temperature, time and pressure for each fraction would give much better results with respect to the yields of gasoline and coke formation. On the other hand, the use of more severe

conditions for cracking low-boiling fractions would increase the octane number of cracked gasoline.

Selective cracking is not confined to any particular method of cracking. The selective cracking of a given fraction may be performed in in mixed- or vapor-phase, non-catalytically or catalytically. The combination of these methods, for instance mixed-phase cracking for heavier fractions and vapor-phase cracking for lighter fractions, may be used in the same unit.

The method of selective cracking has been employed more and more widely during recent years. A primitive modification of selective cracking is performed in two separate operations. A crude oil or residuum is cracked under comparatively mild conditions; this results in a moderate yield of cracked gasoline, and in an appreciable decomposition of heavy viscous fractions (viscosity breaking). The cracking temperature in this stage is about 475°C. (887°F.) and the cracking time is short, ensuring complete absence of coke formation. The pressure used is high enough (from 200 to 500 pounds per square inch gauge) to keep a greater part of the product in the liquid phase. The recycle stock is cracked under more severe temperature-time conditions, the temperature being up to 530°C. (986°F.). Pressures up to 750 pounds per square inch gauge are employed in this operation. The recycle stock consists of a number of uncracked straight-run and cracked distillates which are processed non-selectively.

In the further development of selective cracking, the recycle stock is separated into two or three fractions. The heavy fraction (particularly from the flash chamber or evaporator) may be blended with the virgin crude or residuum and cracked in the viscosity breaking operation. The distillates from the bubble tower, straight-run and cracked, are separated into two fractions, one of which includes low-boiling products, such as heavy naphtha or light kerosene, boiling approximately in the range 175-275°C. (347-527°F.). The other fraction consists of heavier gas oil boiling approximately in the range 250-350°C. (482-662°F.). The naphtha fraction is cracked or reformed at temperatures from 500°C. to 550°C. (932-1022°F.) and pressures of about 500 pounds per square inch gauge. The cracking may be carried out in a once-through operation. Recycling is not necessary in this case since the fractions consist, in addition to paraffins and olefins, of mono- and bicyclic naphthenes and aromatics which are condensed and form coke only under very severe cracking conditions.

In the recycle operation the gas oil fraction is cracked at a temperature of about 530°C. (986°F.) and a pressure of 300 to 750 pounds per square inch gauge. Vapor-phase cracking at high temperatures up to 600°C. (1112°F.) and low pressures can also be used in this scheme of selective cracking. The lighter fractions of gas oil with a comparatively low end point may be selected for the vapor-phase process, the other gas oil fractions being cracked in the mixed-phase operation.

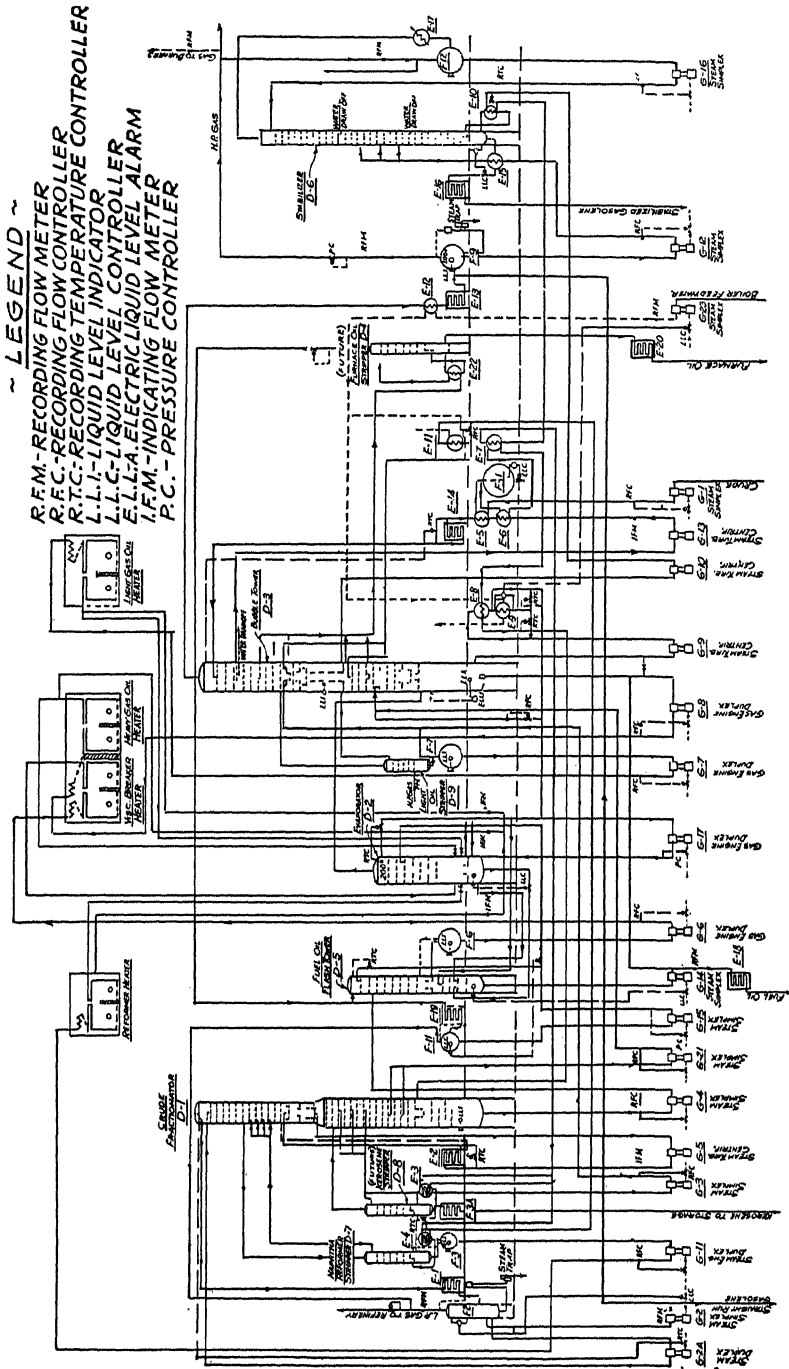
The fractions may be selected on the basis of the boiling range and origin, *i.e.*, the straight-run fractions may be cracked separately from the recycle stocks. A logical development of this method would involve the separation of the charging stock in a series of straight-run and recycle fractions and the cracking of each of these fractions under selective conditions of temperature, time and pressure. The advantages of selective cracking, however, would be more than counter-balanced by the difficulties in design and operation. In commercial practice, the possibilities of selective cracking are severely limited by the reasonable number of the fractions to be processed.

The method of cracking crudes and straight-run residues in two operations (viscosity breaking and cracking of distillate or clean oil) was originally introduced in refinery practice as a combination of straight-run distillation and cracking. In such combination units the waste heat of cracking is utilized for distillation of crude or residuum. Thus, in addition to more favorable selective cracking conditions for crude and distillates, this method of cracking gives a considerable saving in initial investment and operation expenses. The units of this type have been specified as combination units. As further developed, the combination units use more and more the method of selective cracking, with separation of various fractions which are processed under selective cracking conditions. As a matter of fact, the modern units are a combination of straight-run distillation, distillation of synthetic crude and selective cracking.

A combination selective Kellogg cracking unit of the Atlantic Refining Company has been described by Williams.⁵⁷ The cracking is carried out in four sections of two tube stills. The reduced crude is mildly cracked at a moderate temperature of about 870°F. at the outlet of the coil (visbreaking). The distillates are separated into three fractions: heavy gas oil, light gas oil and heavy naphtha. The heavy gas oil, including the flash distillate (produced in a vacuum flash chamber at 75 mm. pressure) and the visbreaker bubble tower bottoms, is cracked in a coil at a temperature of about 950°F. at the outlet. The light gas oil, including the gas oil from the crude flash tower, the visbreaker gas oil and the gas oil from reforming, is processed in a coil at temperatures up to 1000°F. at the outlet. Finally, the naphtha from the crude flash tower is cracked in the coil at temperatures up to 1000°F. at the outlet. All processes are performed under pressures not specified in the article.

The operation of a Lummus selective cracking four-coil unit is described by Smoley, Mekler and Schutte,⁴² and summarized in Table 64. The scheme of a similar unit is given in Figure 5, which is self-explanatory.

Selective cracking is performed in as many heaters as there are stocks to be selectively cracked. It is understood that in some cases the separate heaters can be replaced by separate sections in the same heater (Chap-



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 5.-Lummus Combination (Selective Cracking).

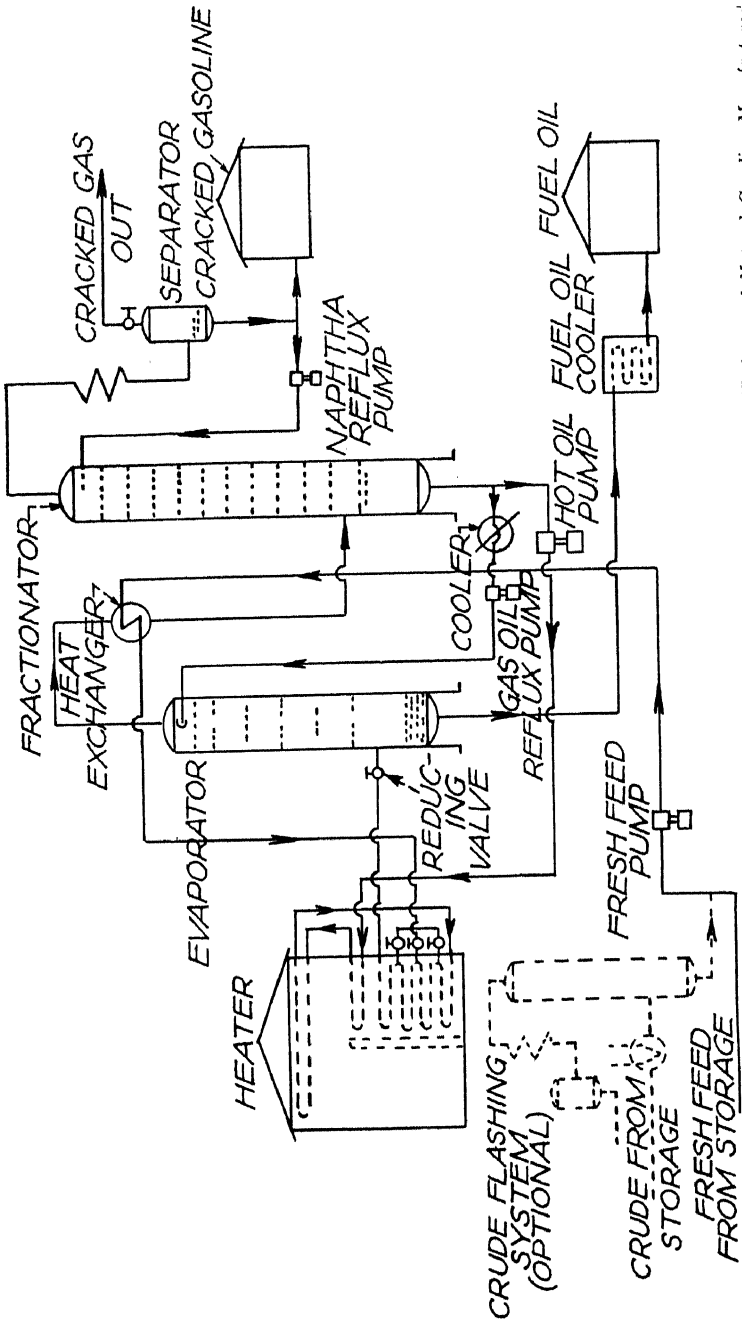
Table 64. Operation of Selective Four-Coil Unit.

Crude A.P.I. Gravity	36.9-39.9
1. Visbreaker Heater	
Throughput B/D	4160-5500
Feed gravity, A.P.I.	19.2-21.2
Outlet temperature (°F.)	880
Outlet pressure (lbs./sq. in.)	235-250
2. Heavy Oil Heater	
Throughput B/D	4010-4330
Feed gravity, A.P.I.	19.3-23.6
50 per cent at °F.	542-563
90 per cent at °F.	650-673
Outlet temperature (°F.)	925-930
Outlet pressure (lbs./sq. in.)	400
3. Light Oil Heater	
Throughput B/D	5870-6030
Feed gravity, A.P.I.	26.8-31.2
50 per cent at °F.	445-454
90 per cent at °F.	503-515
Outlet temperature (°F.)	980-995
Outlet pressure (lbs./sq. in.)	600
4. Reformer	
Throughput B/D	1760-2010
Feed gravity, A.P.I.	38.8-55.5
50 per cent at °F.	335-474
90 per cent at °F.	416-602
Outlet temperature (°F.)	945-975
Outlet pressure (lbs./sq. in.)	750

ter 4). Two heaters or two heating sections are necessary for the simplest combination unit performing viscosity breaking, accompanied by distillation, and cracking of recycle and other distilled stocks.

The Unicoil injection process is designed to simplify selective cracking and avoid the use of two heaters or heating sections (Figure 6). The clean recycle stock is cracked under comparatively severe conditions, for instance, at a temperature of about 520°C. (968°F.). The soaking time should be sufficient to insure proper conversion of the stock in the radiant tubes. The fresh stock preheated in a heat exchanger is injected into the soaking tubes in the convection section, at a point where the recycle stock has been cracked to the desired extent. The temperature of the mixture of two stocks after injection becomes much lower than that of the recycle stock before injection. Then the temperature gradually increases, when the mixture moves to the outlet of the heater. The final temperature in the outlet should be moderately high, in the neighborhood of 485°C. (905°F.), to produce a suitable conversion or viscosity breaking of fresh stock without, however, any appreciable coke formation. Further cracking of the recycle stock does not take place in practice under these comparatively mild conditions. The Unicoil injection process is used mostly for cracking units of small capacities.

As has been shown above, the production of selective fractions is carried out by distillation of straight-run and cracked stocks. There are some patents covering the selective cracking of fractions produced by treatment with solvents.



Courtesy "Refiner and Natural Gasoline Manufacturer"

Fig. The Un. P.

Catalytic Cracking

The special catalytic processes, such as polymerization, alkylation, hydrogenation and dehydrogenation, are discussed in Chapters 1 and 3, while this section is confined to the catalytic cracking of gas oils and similar charging stocks.

The development of catalytic cracking has long been hampered by improper choice of catalysts. It should be borne in mind that the use of catalysts as accelerators of thermal cracking reactions cannot be justified from the commercial standpoint. Without catalysts, the rate of cracking reactions is very high at reasonable temperatures, and can be easily controlled by proper choice of cracking conditions, particularly temperature.

Most catalysts affect the rate of cracking reactions to a very moderate extent, and, as a result, the temperature conditions of catalytic cracking are rather close to those of the thermal process. Moreover, such metallic catalysts as nickel, etc., accelerate many undesirable reactions of the decomposition of hydrocarbons to carbon and hydrogen or carbon, methane and hydrogen, as has been explained in Chapter 1.

Otin and Savencu³⁶ investigated the action of various catalysts on the cracking of a kerosene of specific gravity 0.801 at 20°C., and boiling range from 139 to 295°C. in Engler distillation. The temperature of the experiments varied from 100 to 254°C., the pressure from 1 to 20 atmospheres, and the time was two hours in all experiments. The Engler distillation and the chemical composition of the kerosene were tested after each cracking experiment. Various metals (potassium, sodium, magnesium, zinc, nickel, tin, iron and aluminum), oxides (calcium, magnesium, zinc, iron, chromium and aluminum), chlorides (potassium, sodium, calcium, magnesium, zinc, iron, chromium and aluminum) and sulphates were used as catalysts in the amount of 5 per cent by weight on the kerosene. With the exception of aluminum chloride, the yield of decomposition products was very small with all these catalysts. Under the most severe conditions employed (200-250°C.) and for two hours, the yield of the fraction to 150°C., 3 per cent in the original product, was either unchanged (3 per cent) or increased to 4-6 per cent, and to 8 per cent in the case of ferric chloride. Only in the presence of aluminum chloride did the amount of this fraction increase to 34 per cent.

The change in the chemical composition of the kerosene after treatment also was not significant. In some cases, however, the percentage of olefins appreciably decreased and that of aromatics increased. Thus, in the presence of calcium and magnesium oxides the percentage of olefins fell from 11.8 to 5-6 and that of aromatics rose from 6.4 to 11-12.

The catalytic action of aluminum chloride on the cracking of petroleum products is unique and is not comparable to that of any other catalyst. McAfee³⁰ described the process as early as 1915. The aluminum chloride process is performed at low temperatures of about 250-280°C.

(482-536°F.) and at atmospheric pressure in the presence of 2 to 10 per cent of anhydrous aluminum chloride. Since aluminum chloride is insoluble in oils, the mixture of oil and catalyst is stirred in a still at the cracking temperature. The cracking gradually proceeds, producing cracked gasoline and other, heavier decomposition products. The products of decomposition are conveyed to a cooler, where high-boiling oils are back-trapped into the still for repeated cracking. The process extends over a period of 24 to 48 hours. The operation is interrupted when only high-boiling fractions are left in the still. The reactions of condensation take place simultaneously, resulting in the formation of coke, as in conventional cracking. The yield of coke depends upon the nature of the cracking stock and the yield of gasoline.

Yields of gasoline can be obtained up to 60 per cent with aluminum chloride, if gas oils are used as charging stocks. The process was in commercial use for a few years by Gulf Refining Oil Company.

It should be emphasized that the aluminum chloride process was developed during the earlier years of commercial cracking, when the use of high temperatures and high pressures was thought to be dangerous. Further development of thermal cracking overcame the difficulties encountered in the high temperature-pressure operation. At the present time the advantages of the low temperatures and pressures of the aluminum chloride process are more than counterbalanced by the cost of the catalyst, the corrosive action of hydrogen chloride, coke formation and other drawbacks.

The use of certain adsorptive materials, such as various clays, as catalysts in cracking seems to be more promising. This is not new and has been described in many patents, the most important of which are described below.

Thiele and Cordes⁴⁷ in 1923 patented the use of hydrosilicates containing more than 5 per cent free hydrosilic acid, such as floridine. The catalyst may be used in granular form in the amount of 25 per cent of the product or more. The catalyst is located in the dephlegmator of a still in which the product to be cracked is distilled. In the same year Erdoel and Kohlenverwertung Gesellschaft¹¹ covered the use of various catalysts, including pumice and hydrosilicates. The cracking takes place in a batch provided with a screen support for the catalyst.

Erlenbach¹² uses chemically neutral substances having great physical adsorption capacity, such as pumice and hydrosilicates, as cracking catalysts. The oil is circulated through a fairly deep layer of catalyst on a perforated support within the still. Goux¹⁵ employs pumice, bleaching clay and silicates of alumina with a small amount of oxides of heavy metals (nickel, cobalt, copper, iron, etc.). The catalyst is used in small pieces. The process is performed at a temperature of 425-575°C. in the vapor-phase.

According to Leamon,²⁷ the catalytic cracking is performed in a cracking zone, including a mass of porous adsorptive material (such as

silicates of alumina), heated to cracking temperature. The vapors to be cracked are conducted through the cracking zone.

Houdry¹⁹ patented the use of hydrosilicates containing 70-80 per cent of silica, 20-10 per cent alumina, not over 10 per cent other oxides and particularly not over 3 per cent ferric oxide. Other oxides, such as nickel oxide, may be added in an amount not over 10 per cent. The catalyst is used in rigid form adapted for frequent regenerations by oxidation with air without substantial loss of activity. In another patent²⁰ Houdry discloses the composition of hydrosilicate as conforming to the ratio of silica to alumina from $3\frac{1}{2}:1$ to $4:1$. A small amount of a manganese compound, about 1 per cent, is added to the catalyst to facilitate regeneration. In addition to natural or activated silicates of alumina, some highly active synthetic silicates may be used as cracking catalysts.

The Houdry process was described by Houdry, Burt, Pew and Peters.²³ The catalyst used in the Houdry process, conforming to the composition disclosed above, is molded under pressure, dried and baked. The catalyst chambers provide an efficient and uniform contact of the vapors with

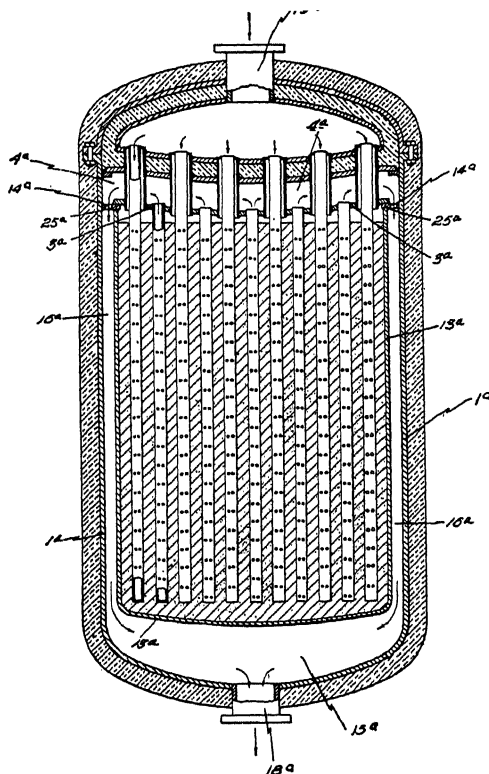


FIGURE 7.—Houdry Catalytic Chamber.

the catalytic mass. Figure 7, for instance, shows the arrangement of a catalytic chamber according to Shabaker *et al.*⁴¹ The vapors enter the catalyst mass through openings in the inlet tubes extending into the mass and leave through openings of the outlet tubes, as shown in the drawing.

The activity of the catalyst is rapidly decreased during the operation due to the deposition of carbonaceous materials. The operating cycles vary from 20 to 135 minutes in cracking gas oils. Regeneration of the catalyst is performed by oxidation with air at moderate temperatures. Regeneration restores the original activity of the catalyst, and the actual operation of the same catalyst lasts over a year. According to Houdry,²² the coke deposit should be below 15 grams per liter of catalyst to secure maximum yields and reduce the regeneration periods to 40 minutes or less. Temperature control is of paramount importance in catalytic cracking and particularly in the regeneration operations, which liberate a considerable quantity of heat. An excessive temperature of regeneration, exceeding 1000-1050° F., impairs the activity of catalyst. The difficulties of properly controlling the temperature in the presence of adsorbent materials, which are poor conductors of heat, have been overcome by the use of efficient heat exchange media such as fused salts, molten metals and alloys, etc., which are circulated in the tubes located in the catalyst chamber.

The heat produced in regenerating the catalyst by burning the carbonaceous deposits is recovered as steam and electric power; and this power is sufficient for the electric and steam requirements of the cracking unit.

The original catalyst cost for a plant of a capacity 15,000 barrels per day has been given as about \$36,000.00.

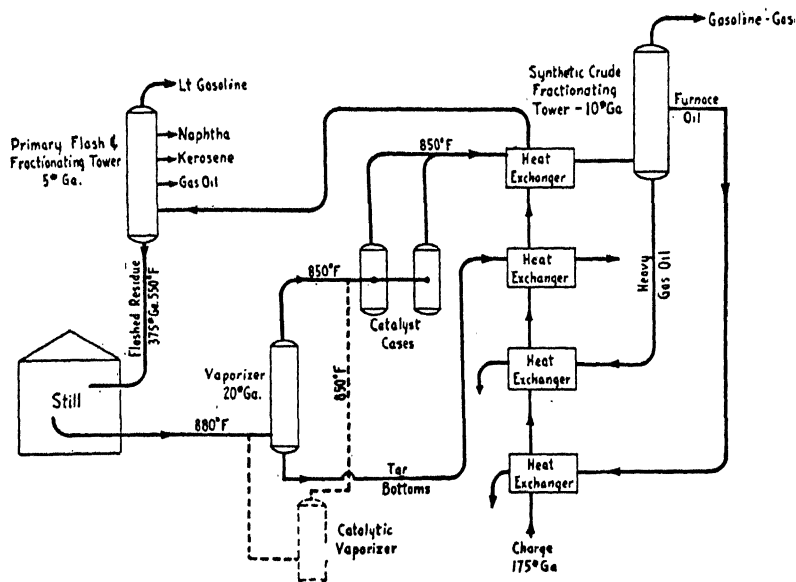
Figure 8 represents the general scheme of the process. It is carried out under low pressures of about 30 pounds per square inch gauge. Crude oil is pumped through heat exchangers to a primary flash and fractionating tower, where the desired straight-run products are removed. The residue from the primary flash tower enters a pipe still where it is heated to approximately 470°C. (880°F.). From the pipe still the residue is conveyed to a vaporizer. In the vaporizer the bottoms are separated from the evaporized fractions which pass to the catalyst chambers. The separation of the cracked products leaving the catalytic chamber is the same as in other cracking processes.

In the non-residuum process (shown by dotted lines in Figure 8) a catalytic vaporizer replaces the vaporizer mentioned above. As a result, the heavy constituents of the residuum-yielding tar are completely decomposed in the presence of the catalyst to coke and distillates which are passed into the catalyst chambers.

The cracking is carried out in a once-through operation. A high yield of gasoline per pass up to 45 per cent is accompanied, due to a high conversion, by an appreciable coke formation, from 1 to 5 per cent with reference to the charge. On the other hand, the gas formation is very

moderate, from 4 to 7. per cent by weight, less than can be expected on the basis of the above conversion. This may be explained either by secondary reactions involving the gases formed, or by the direction of decomposition reactions to the middle of paraffin chains.

The throughput of gas oil in Houdry units equals approximately 1 volume of gas oil per 1 volume of catalyst per hour or more. The



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 8.—Flow Chart of Houdry Catalytic Cracking.

rate or the reaction time predetermines the properties of the gasoline, as will be seen later.

The cracked residuum, in the customary meaning of this term, is not formed in the Houdry process due to the fact that clay has a decarbonizing action which decomposes the asphaltic constituents to coke and gas oil. A considerable portion of the catalytic gas oil may be used as furnace oil.

The catalytic gas oils can be cracked repeatedly by catalytic operation, producing lower yields of gasoline than those obtained with virgin straight-run oil. In the second pass the yield of gasoline is about 30 per cent and in the third pass about 25 per cent of the charge, as can be calculated from Table 6 of the original article.²³ Thus, the thermal and catalytic stability or refractoriness of the recycle stocks increases with increasing operation, as in thermal cracking.

Catalytic gas oils can be successfully used as charging stocks for thermal cracking, producing high yields of gasoline. It should be kept

in mind that the Houdry recycle stocks have a distinctly aromatic or hydroaromatic character. Due to their refractoriness, they are only slightly cracked under the mild temperature conditions of the Houdry process. High-temperature thermal cracking is more suitable for breaking down the cyclic hydrocarbons of Houdry recycle stocks. Due to low yields of cracked gas and moderate coke formation, the total recovery of liquid products, gasoline and gas oil, is great, from 96 to 100 per cent by volume.

The summarized and selected data on the Houdry process are given in Tables 65-67. As the figures of Table 67 show, coke and gas formation in the catalytic non-residuum process is more moderate than in thermal non-residuum cracking.

Catalytic cracking produces gasolines having a small content of sulphur. The sulphur content in raw cracked gasolines does not exceed 0.1 per cent, when charging stocks contain 1 per cent of sulphur or less. For charging stocks high in sulphur (about 2 per cent), the sulphur content in catalytically cracked gasolines increases to 0.2 per cent. The desulphurizing action of the catalyst in cracking should be mentioned.

Table 65. Yields of Cracked Products in the Houdry Process.

One Pass; Charging Stock: Gas Oils.

Origin of Gas Oil	Mid-continent	W. Texas-N. Mexico	E. Texas	Coastal
Charging Stock				
A.P.I. Gravity	37.8	30.4	34.5	30.0
I.B.P. (°F.)	416	440	420	406
50% (°F.)	536	554	574	494
E.P. (°F.)	656	683	750	602
Cracked Products				
Dry Gas (% by wt.)	4.3	5.2	6.1	4.9
Catalyst deposit (% by wt.)	3.3	4.0	3.2	1.0
Gasoline, at 400°F. E.P. (% by vol.)	44.7	41.6	44.4	50.3
Catalytic gas oil (% by vol.)	53.0	55.3	51.9	49.9
Liquid recovery (% by vol.)	97.7	96.3	96.3	100.2

of Cracked Products in the Houdry Process.

Pass; Charging Stocks: Crudes.

Crude	E. Texas*	E. Texas†	B Coastal*	36 A.P.I. M.C.*	36 A.P.I. M.C.‡	Lagunillas, Entire Crude
Charge to plant (% crude)	58.5	38.0	75.6	66.7	52.4	100
Tar (primary flash tower)						
% vol. of crude	8.0	8.0	6.0	8.4	8.4	35.4
A.P.I. gravity	12.6	12.6	12.8	13.3	13.3	4.2
Charge to catalyst:						
% vol. of crude	50.5	30.0	69.6	58.3	44.0	64.6
A.P.I. gravity	29.0	23.9	26.8	30.0	27.7	25.2
I.B.P. (°F.)	452	508	415	420	538	182
50% (°F.)	690	740	615	650	711	672
E.P. (°F.)	760+	760+	760+	760+	760+	760+
Cracked products:						
Dry gas (% by wt.)	4.5	5.1	7.0	4.0	5.4	3.8
Catalyst deposit (% by wt.)	5.3	5.4	4.4	3.9	3.5	4.5
Gasoline, 400°F. E.P. (% by vol.)	44.0	42.6	47.2	41.9	44.1	44.5
Catalytic gas oil (% by vol.)	54.4	56.4	49.2	57.7	54.9	54.7
Liquid recovery (% by vol.)	98.4	99.0	96.4	99.6	99.0	99.2

* Topped of naphtha.

† Topped of naphtha-furnace oil.

‡ Topped of naphtha and kerosene.

Note: Per cent of cracked products are given with reference to the charge to catalyst.

Table 67. Yields of Cracked Products in the Houdry Process.
One Pass; Non-Residuum Operation.

Crude	M.C. 17% Crude Bottoms	Lagunillas 100%	W. Texas and N. Mexico, 35% Bottoms
Charge to Catalyst			
Per cent of crude	17.5	100	35.0
A.P.I. gravity	17.8	17.3	17.1
I.B.P. (°F.)	550	160	576
50% (°F.)	760+	760+	731+
Cracked Products			
Dry Gas (% by wt.)	5.0	4.3	3.9
Catalyst deposit (% by wt.)	13.8	11.9	7.8
Gasoline 400°F. E.P. (% by vol.)	47.7	44.9	39.4
Catalytic gas oil (% by vol.)	46.1	50.0	58.8
Liquid recovery (% by vol.)	93.8	94.9	98.2

Catalytic cracked gasolines are comparatively stable with respect to the gum formation due to the polymerizing action of clay upon the unstable unsaturated hydrocarbons responsible for the gum-forming properties of gasolines. As a result, catalytically cracked gasolines can be used as aviation fuels after a light treatment by sulphuric acid or by clay at a high temperature.

Voorhis^{49b} described a new 15,000-bbl. Houdry unit of the Magnolia Petroleum Company. The crude oil (Mirando) is preheated in a series of heat exchangers, including the exchange against the heat transfer medium, molten salts, used in the process. At a temperature of 470°F. the crude oil, split in two parallel streams, passes through an Alcorn furnace, where the temperature of the charge is raised to 825°F. The inlet pressure to the furnace is 175 pounds per sq. in. and the outlet pressure is 75 pounds. The heated charge passes to the vaporizer after having 8 per cent by weight of superheated steam added. Evaporation and separation of tar in the vaporizer takes place at 800-825°F. and 40 pounds' pressure. Vapors from the vaporizer are passed to the special radiant side of the Alcorn furnace and heated to 880°F. The vapors from the furnace finally pass to one of the three pairs of catalyst cases maintained at 900°F. and 30 pounds' pressure. Leaving the cases, the vapors pass through the heat exchangers to the main fractionating power at 734°F. and 25-28 pounds' pressure. The main fractionating tower and an auxiliary tower separate gasoline, light gas oil (fuel 2) and heavy gas oil.

The catalyst cases are 10 feet 7 inches in inside diameter and 38 feet in over-all height. As has been mentioned above, the temperature in the cases during cracking and regeneration is controlled by the circulation of a heat transfer medium, a eutectic mixture of salts. This mixture, having a melting point of about 300°F., is maintained above 370°F. during circulation. The molten salt is a much more effective heat transfer medium than steam, which was used in earlier Houdry units. At the present time each pair of cases is in operation ten minutes; regeneration lasts ten minutes, and preparation for operation and regeneration requires five minutes each.

In addition to the conventional heat exchange, the unit has two

special features. The salt mixture, heated to a high temperature during the regeneration of the catalyst, is pumped through the special heat exchangers counter-current to water and generates steam under 450 pounds' pressure. The combustion gases produced in regeneration are passed to the second combustion case in which, by means of a catalyst, total combustion to carbon dioxide and water is effected. The combustion products then are utilized in the Brown-Boveri hot-gas turbine, directly coupled to the compressor which compresses the air for regeneration.

The single-pass operation of the Houdry unit on Mirando crude gives the following yields:

Stable gasoline	33.3 per cent
No. 2 fuel	32.6 " "
Heavy gas oil	17.4 " "
Tar	12.7 " "
Gas and losses	4.0 " "

Gasoline 44° A.P.I. and No. 2 fuel 24° A.P.I. (boiling range 446-683° F.) are the principal products of the operation. Gasoline requires sweetening only. Octane number of the gasoline is 78 by the Motor Method and 81-82 by L-3 Method.

The comparative data on the utility requirements for conventional thermal cracking and the Houdry process are as follows:

Material	Thermal Unit (units/bbl. of gasoline)	Houdry Unit (units/bbl. of gasoline)
Gas (B.t.u.)	416 M	554 M
Steam (pounds)	207	46
Electricity (kwh.)	4.30	4.28
Water (gal./min.)	2.21	1.92

The comparative data on the equipment requirements are summarized in the table:

Type of Equipment	Thermal Unit (units/bbl. of gasoline)	Houdry Unit (units/bbl. of gasoline)
Sq. ft. of heat exchanger surface	3.24	5.87
Sq. ft. of condensing and cooling surface	2.54	3.34
Oil pump cap'y installed, B/D	48.44	29.20
Salt pump cap'y installed, B/D		178.96
Water pump cap'y for steam generation, installed, B/D		8.90
Total installed pump cap'y, B/D	48.44	217.06
% of total pump cap'y actually used	48.7	54.3
Sq. ft. of heater tube surface	3.494	2.022

A considerably greater pump capacity, catalytic chambers, regeneration equipment, etc., cause a higher first cost of the catalytic units as compared with conventional cracking units. According to Voorhis, the cost of the 15,000-bbl. Houdry unit is \$2,980,000 or about \$200 per barrel of daily capacity.

The Houdry process, using activated clay as a catalyst, is performed at a temperature of 475°C. (887°F.) or, in other words, at temperatures which are not much lower than are used in thermal non-catalytic processes. As might be expected, the catalytic action of the activated

clay on the decomposition reactions is moderate. The main action of clay, however, probably takes place in the secondary stages of cracking, involving the olefins formed in the first stage of the process. The isomerizing, polymerizing and alkylating action of clays has been repeatedly mentioned in Chapter 1. Under the catalytic action of activated clays the olefins are isomerized, producing iso-olefins. According to Egloff *et al.*,⁸ the isomerization of olefins in the presence of clay precedes decomposition, resulting in the formation of low molecular olefins of branched structure. Olefins are easily polymerized at high temperatures in the presence of clay. The alkylation of aromatics and paraffins with olefins is not improbable in the presence of activated clays. The comparatively moderate temperatures used in the Houdry process are favorable to alkylation.

The alkylation reactions of paraffins, yielding branched paraffins, seem to be of particular importance. As a result, the content of olefins and other unsaturates in Houdry gasolines is usually much lower than for ordinary cracked gasolines. It is of interest that the acid heat of a Houdry gasoline 68 can be reduced to 9-21 by further treatment by the same process in the presence of clay. However, the content of unsaturates in Houdry gasolines depends upon the conditions of the process, particularly upon the reaction time. The unsaturation may be high at higher temperatures and especially with short reaction (contact) times. Under these conditions the extent of secondary reactions, involving unsaturates formed, may be very limited. When the reaction time is short or the throughput is great, the unsaturation (iodine number or acid heat) of Houdry gasolines can be as high as that of thermally cracked gasolines. This evidently shows that the secondary reactions induced by clay require much more time than the primary decomposition reactions catalyzed by the same catalyst. It is of particular interest that the octane numbers of more saturated Houdry gasolines do not differ appreciably from those of less unsaturated ones. The reaction time should be greater for the production of more stable aviation gasolines and shorter when motor gasolines are manufactured.

The Houdry gasolines boiling in the range of aviation gasolines have an octane number around 78 by A.S.T.M. Motor Method, and a low specific gravity. The latter shows that the gasolines do not contain a high percentage of aromatics. Thus, the high octane numbers of the Houdry gasolines should be attributed principally to the branched paraffins produced as a result of alkylation under the catalytic action of clay. It is also probable that the highly branched olefins formed in the process play an important part in the antiknocking properties of Houdry gasolines.

A Houdry gasoline was treated with sulphuric acid (2 volumes per 1 volume of gasoline) to remove aromatic and unsaturated hydrocarbons. After the treatment the gasoline was redistilled to the original end point. The results are summarized as follows:

	—Houdry Gasoline—	
	before treatment	after treatment
Specific Gravity at 15°C.	0.733	0.704
A.P.I. gravity, 60°F.	36.6	61.8
Iodine number	46	0
Octane number (S.F.R. Motor)	77.3	68.2

The treated gasoline consists approximately of 65 per cent paraffins and 35 per cent naphthenes (Chapter 5). This proves that the paraffins of Houdry gasolines are of a comparatively high octane number or, in other words, belong to highly branched paraffins.

A strong dehydrogenation of naphthenes is probable under the conditions of the Houdry process, resulting in a higher content of hydrogen in cracked gases and in a higher aromaticity of gasoline, as compared with conventional cracking at moderate temperatures (Chapter 5).

Thus, in comparison with thermal cracking, the conditions of the Houdry catalytic process are comparatively mild, resulting in small gas formation and great recovery of liquid products. The catalyst has apparently a very strong effect upon the secondary reactions, yielding gasolines comparatively stable and rich in branched paraffins. The catalytic condensation of polycyclic compounds produces coke and gas oils instead of the cracked residues of thermal cracking.

The production of high-octane and comparatively stable gasolines is the main advantage of the Houdry process. The additional expenses in conjunction with the use and regeneration of the catalyst may be justified only by the outstanding qualities of gasoline.

The discontinuity of catalytic cracking, employing regeneration *in situ*, is a serious drawback with reference to the effective operation of catalytic chambers. Foster^{13a} reports on the continuous operation of some catalytic units employing a continuous charge and discharge of catalyst, not disclosing, however, any details of the process. It should be mentioned that the continuous charge and discharge of clay has been used in the Stratford gasoline treating process, as will be seen in Chapter 6. The same or another scheme of operation may be used in catalytic cracking.

Berl and Lind¹ investigated cracking in the presence of activated carbon. The cracked gases in the catalytic process are richer in hydrogen and poorer in olefins than in the case of non-catalytic cracking. The cracked gasolines produced with activated carbon are more paraffinic and less olefinic than those obtained in the non-catalytic process. These results show that alkylation of paraffins with olefins, as well as dehydrogenation reactions producing hydrogen, readily occur under the catalytic action of activated carbon. Thus, there is a close similarity between the catalytic action of activated clay and that of activated carbon in cracking.

Another method of catalytic cracking, being developed by U. O. P., has been described by Ziegenhain.⁶⁰ The nature of the catalyst has not been disclosed. The process takes place in the vapor-phase over a catalyst at

temperatures ranging from 500-540°C. (932-1004°F.) or higher, and under pressures close to atmospheric. The yield of gasoline per pass is high, about 30-40 per cent by volume. The catalyst is rugged and can be completely restored by regeneration. As a typical charging stock, a gas oil of A.P.I. gravity 36.7 and boiling range from 407 to 750°F. was used. The total yield of cracked gasoline was 85 per cent, including catalytic polymers produced from cracked gases. The total balance is as follows:

Gasoline	85 per cent
Unpolymerized gas	9 " "
Residuum (25° A.P.I. gravity)	6 " "

Octane number of the gasoline, including the polymers, was 81. The response to tetraethyllead is poor.

The composition of cracked gases before polymerization was:

Hydrogen	15.9	Propane	5.1
Methane	18.5	Iso-butene	8.8
Ethene	4.8	n-Butene	12.3
Ethane	5.2	Butanes	5.0
Propene	21.5	Oxygen, Carbon Monoxide and Nitrogen	2.9

An alternative operation may be run to produce up to 5 per cent iso-octenes in a once-through operation or 12.5 per cent in a recycle operation. The iso-octenes are hydrogenated to iso-octane. This shows that the formation of gases is comparatively large in this catalytic process, and an appreciable part of the total gasoline yield given about (85 per cent) is due to polymerization of the cracked gases formed.

Another type of catalytic cracking and reforming is being developed by a group including the I.G. Farbenindustrie in Germany, the Standard Oil of New Jersey, the Standard Oil of Indiana, and the Kellogg Company. However, no data on the operation and catalysts used in these processes are available.

The cracking catalysts discussed above are solid substances immiscible with the charging stock. Thus the catalysis is heterogeneous. Very little is known of the homogeneous cracking catalysts or, in other words, of the gaseous substances which catalyze cracking reactions at elevated temperatures. According to Varga and Almasi,^{49a} higher yields of low-boiling fractions are produced in destructive hydrogenation from straight-run residues in the presence of 0.25 per cent iodine. There are patents claiming that cracking in the presence of chlorine or chlorinated organic compounds, such as carbon tetrachloride, etc., may be carried out at lower temperatures or with greater yields as compared with the non-catalytic process [for instance, A. J. van Peski, German P. 548,982 (1928); H. Tropsch, U.S.P. 2,063,133 (1936)]. Story claims the use of 1/2 to 1 per cent of oxygen to accelerate the cracking of stocks mixed with C₃ and C₄ hydrocarbons [U.S.P. 2,178,329 (1939)].

Hydrocarbons can also catalyze the decomposition of other hydrocar-

bons. Hessels, van Krevelen and Waterman^{18a} investigated the cracking of methane induced by halogen derivatives, sulphur compounds and hydrocarbons. The experiments were carried out mostly at 1170°C. (2138°F.) and a contact time of 0.07 second or less. Under these conditions methane alone, in the absence of an inductor, passes the heating zone unchanged. The decomposition is appreciable in the presence of halogen and sulphur compounds as well as of aliphatic hydrocarbons, such as propane, butane or olefins. Unsaturated and aromatic hydrocarbons are produced in the process. Aromatic hydrocarbons (benzene or naphthalene) are inactive and do not induce the cracking of methane under the conditions mentioned above. The inductor effect is more pronounced if the concentration of the inductor is smaller in comparison with the concentration of methane.

As a result, the repeated cracking of methane produces an autocatalyzing effect. The paraffins and olefins formed in the first process catalyze or induce the decomposition of methane in the succeeding repeated operations.

Cracking by Partial Oxidation

In conventional cracking the heat required for the process is transferred to the product indirectly through the walls of tubes or reaction chambers. The source of heat is located outside of the product processed. On the other hand, the heat required for cracking may be supplied directly by the partial combustion or oxidation of the product. It should be borne in mind that the consumption of fuel in cracking is comparatively small, amounting to 5-10 per cent with reference to the charge. Thus, theoretically, the combustion of 5-10 per cent of the product processed *in situ* may be sufficient to crack the remaining part (95-90 per cent). The combustion, however, may be incomplete, producing partially dehydrogenated or oxidized hydrocarbons. In this case a greater percentage of the product will be subjected to oxidation, but the products of partial oxidation or dehydrogenation may be incorporated into fuels produced.

The idea of cracking by partial oxidation is not new, and various modifications of this method have been described in many patents.

Dubbs⁶ covered the general idea of the method in question as early as in 1914: ". . . passing air through hydrocarbon when initially heated to a temperature at which the oxygen of the air will react on the hydrocarbon, then continuing the operation by passing through hydrocarbon a sufficient quantity of air to cause by the chemical action alone the desired temperature for maintaining the necessary reaction, without the agency of any substantial external application of heat, and regulating the temperature required for the reaction by regulating the quantity of air passed into hydrocarbons."

According to Biggins,² a little air is given to the cracking zone, thereby keeping up the temperature by the development of heat of oxidation in-

ternally. Reid³⁷ recommends that high-boiling oils be cracked by oxidation at a temperature between about 350 and 500°C. with air disseminated throughout the oil in a state of extremely fine subdivision, obtained by means of a high-speed stirrer. Many other patents relating to the same method might be cited, such as for instance, Burk, R. E., U.S.P. 1,963,647 (1934); 1,989,737 (1935); Burk, R. E. and Hughes, E. C., 1,997,482 (1935); Peck, E. B., and Kleiber, C. E. 1,981,826 (1934), and others.

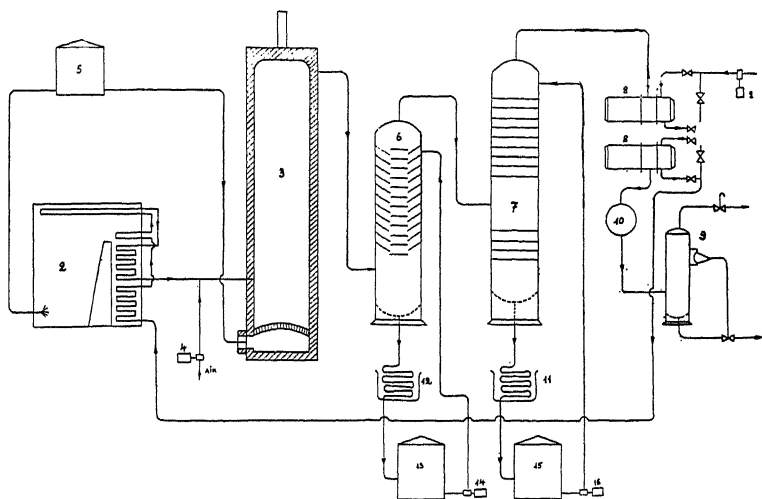


FIGURE 9.—The Dubrovai Cracking Process.

All these methods, however, did not find commercial application in this country. Dubrovai⁵⁰ developed a similar method in the U.S.S.R. which is being used commercially. At least one Dubrovai unit of 100 tons daily capacity is in commercial exploitation.

Figure 9 represents the flow sheet of the Dubrovai process. The product to be cracked is subjected to preliminary heating in a pipe still up to about 450°C. (842°F.), and then passes to a reaction chamber or generator, which air also enters. The pressure is atmospheric. As a result of oxidation, the temperature in the generator rises to 520-550°C. (968-1022°F.). The quantity of air introduced into the generator is about 250 cubic meters for the unit of 100 tons daily capacity. Light gas oils and kerosenes are cracked without coke or soot formation. The gas oil for the experiments described below had the following properties: specific gravity 0.853 and boiling range from 206-360°C. (403-680°F.). The following yields are reported:

Cracked gasoline	55-65 per cent by weight
Residuum	20-15 " " " "
Gas and loss	25-20 " " " "

The gas includes the fuel consumption in the process.

The chemical composition of the cracked gases is as follows:

Olefins	15-20	per cent by volume
Paraffins	8-15	" " " "
Hydrogen	2-8	" " " "
Nitrogen	45-60	" " " "
Carbon monoxide	2-8	" " " "
Carbon dioxide	0.5-5	" " " "

The presence of a small quantity of carbon monoxide and carbon dioxide in cracked gases should be mentioned.

The following data relate to the chemical composition of cracked gasoline:

Unsaturation	57-60	per cent by weight
Aromatics	21-22.5	" " " "
Naphthenes	11-17	" " " "
Paraffins	0-9	" " " "
Dienes	None	

In addition to hydrocarbons, raw cracked gasolines contain an appreciable amount (about 3-4 per cent) of oxygen compounds, such as peroxides, acids, phenols and aldehydes.

These figures clearly show that complete combustion of the charging stock to carbon dioxide (or carbon monoxide) takes place to a very small extent. The formation of organic oxygen compounds, such as acids, aldehydes, etc., also is of secondary importance. The reactions occurring in the generator are mostly those of dehydrogenation and decomposition, resulting in the formation of unsaturated hydrocarbons, as well as of aromatics and naphthenes of low molecular weight. Cracked gasolines produced by partial oxidation are similar to vapor-phase cracked gasolines with reference to the high content of olefins and aromatics.

Due to the presence of oxygen compounds, and a high content of olefins, the losses in refining Dubrovai gasolines are comparatively high. The first stage of the treatment is washing with caustic to remove acids, phenols and aldehydes. It should be mentioned that the spent caustic contains condensation products of aldehydes and phenols, phenols, etc., which probably may be utilized for the production of plastics.

The second stage of the treatment is carried out by means of zinc chloride. The yields of treated gasoline from the raw product are of about 84 per cent by weight. The final product is stable (induction period 5-10 hours) and of high octane number (about 80) (Waukesha Motor).

The cracked residuum of the Dubrovai process is of high specific gravity (0.965) and of comparatively low boiling range, distilling from 274 to 360°C. (14 per cent bottoms above 360°C.).

The commercial results of the Dubrovai process do not appear to be especially attractive with respect to the yields and qualities of gasoline as compared with thermal or catalytic cracking. On the other hand, the air mixed with the charging stock substantially increases the volume of the charge to be treated. An interesting application of this process is the

ignition and cracking of crude oil *in situ* in the exhausted oil sands. The oil still left in the sands is ignited and partially burned by pumping air into the hole. The oil is released from the sands due to the increase in temperature of the sands as well as the gases produced by oxidation and cracking. This method is being tested in Russia on a semi-commercial scale.

Cracking in Various Media

This section is confined to cracking in the presence of an excess of an inert gaseous product, as a medium of cracking.

Cracking in an inert medium, as well as under low pressure, takes place under lower partial pressures of hydrocarbons than is the case in conventional cracking. From the theoretical standpoint, any substantial effect of the medium upon the monomolecular reactions of decomposition is hardly to be expected. However, a catalytic effect of certain gases on the rate of cracking may be possible. On the other hand, the secondary reactions of polymerization and condensation may be strongly affected by decrease of the partial pressure of cracking products, as will be seen later.

Information on cracking in various media is available, for the most part, in patent literature. Cracking in different media, first of all in the presence of steam (aquolization), was suggested in many early patents.

Greenstreet¹⁶ advocated the use of large amounts of water in cracking petroleum oils at temperatures above 1000°F., employing oil and water in substantially equal proportions, or a great excess of water. Washburn⁵³ recommended cracking kerosene with an equal amount of water, and gas oils with a smaller proportion of water. According to Zerning,⁶¹ a mixture of water and oil, preferably in the proportion of 1 part of water for every 6 to 10 parts of the oil, is conducted under pressure through a still heated to a temperature of 300-400°C., and then through pipes heated to a dark red.

The new patents cover some special features of aquolization; for instance, Ellis⁹ covered the separation of water from oil after aquolization under pressure and the recycling of the hot water to the cracking. Haslam¹⁸ recommended the use of very high pressures, upwards of 100 atmospheres, and high molecular ratios of water to oil, more than 14:1. Forrest *et al.*¹³ increased the molecular ratio of water to oil to 80:1. Ellis¹⁰ advocates cracking petroleum distillates, non-catalytically or catalytically, in the presence of inert gases, such as gaseous hydrocarbons, nitrogen, carbon dioxide, carbon monoxide and the like. The ratio of inert gas to oil is preferably in the neighborhood of 100 to 300 cubic feet (at atmospheric pressure) to 1 gallon of the oil to be treated.

All these investigators claim higher yields and better properties of gasolines and less coke formation when the process is carried out in the presence of various media. None of these processes, however, has commercial application.

Whitham⁵⁹ investigated the cracking of butane in the presence of steam at temperatures of 600-1050°C. Other conditions being equal (temperature and contact time), the content of unsaturates increased with increasing ratio of steam to butane at temperatures from 600-950°C. At temperatures above 1000°C. the gases produced did not contain unsaturates either in the absence or in the presence of water. The data of Table 68 are illustrative of the effect of steam on the formation of olefins.

Table 68. Cracking of Butane, Alone and in the Presence of Steam.

Ratio of Steam to Butane	Temp. (°C.)	Contact Time (seconds)	Liters of Unsaturates Per Liter of Butane
0.0	650	60	0.45
0.3	650	60	0.58
1.3	650	60	0.86
4.3	650	60	0.90

It is evident that the presence of an excess of steam prevents the polymerization and other secondary reactions of olefins formed as a result of cracking.

As has been shown in Chapter 1, the use of vacuum or an excess of steam in thermal decomposition of butane or cyclohexane considerably increases the yields of butadiene. The part played by steam in these reactions is, evidently, the same as in the cracking of butane described above. Butadiene formed at high temperature is protected by low partial pressure or by the molecules of steam from further bimolecular reactions of polymerization and condensation.

The use of inert gases as heat carriers in vapor-phase cracking will be discussed in Chapter 4.

Cracking in the Presence of Hydrocarbon Gases

There are a few patents covering the cracking of liquid petroleum products mixed with hydrocarbon gases. It has been postulated in a number of these patents that hydrocarbon gases rich in hydrogen may react under cracking conditions with liquid petroleum stocks or decomposition products thereof, poor in hydrogen, and may produce higher yields of gasoline, as well as decrease coke formation. The temperature conditions of the process in question do not differ substantially from those of conventional thermal cracking. The pressures recommended are either the same or somewhat higher than in cracking. As a matter of fact, interaction between such gases as methane, ethane, propane and high molecular weight olefins or cyclic hydrocarbons is very improbable under the conditions of conventional cracking from the thermodynamic standpoint. Either much higher temperatures or much higher pressures should be used to bring about the above interaction. Thermal conversion of low molecular weight paraffins is also improbable under conventional cracking conditions. Thus it is not believed that these patents are of practical value.

Another part of the patents in question relates to cracking liquid

petroleum products and polymerizing olefinic gases simultaneously for instance, Wagner, C. R. U.S.P. 2,157,224 (1939); Ruthruff, R. F. 2,166,288 (1939); Mashwitz, P. A. 2,177,146 (1939). As has been stated in this chapter, the temperature-pressure-time conditions of high-pressure cracking and thermal conversion of olefinic gases are rather similar. Thus the simultaneous cracking of gas oils and the thermal polymerization of olefinic gases may be feasible commercially under certain conditions of temperature, time and pressure. The temperature of the process, indicated in these patents, ranges from 850 to 1200°F., and the pressure from 500 to 2000 pounds per square inch. On the other hand, the partial pressure of low molecular weight gaseous olefins in the mixture of gas and cracking stock is low as compared with the thermal polymerization of the gas alone. Thus the conditions for polymerization of gaseous olefins should be considered as less favorable than in the case of thermal polymerization of gases. The interaction of gaseous olefins with products of cracking of gas oil should be of secondary importance, particularly at moderate temperature and pressure conditions. It is believed that the yields of cracked gasoline obtained in this operation should be less than those which can be obtained as a result of cracking gas oil and thermal polymerization of olefinic gases in two separate operations. No reliable experimental data are available on the combination of cracking and thermal polymerization.

COMMERCIAL APPLICATIONS OF CRACKING

The applications of modern cracking are numerous. The production of gasoline from liquid petroleum products remains the main commercial application of cracking. In addition to gasoline, gas, residuum or coke are obtained as by-products. The cracking of liquid petroleum products may be performed either as the residuum process, yielding gasoline, gas and residuum; or as the non-residuum process, giving gasoline, gas and coke. Both processes are carried out at comparatively moderate temperatures not exceeding 600°C. (1112°F.). Cracking petroleum products at higher temperatures above 650°C. (1202°F.) yields mostly aromatic hydrocarbons and may be designated as the high-temperature aromatization process.

Cracking is frequently used for the improvement of properties of heavy viscous residues, naphthas or gasolines. These processes are known as viscosity breaking and reforming.

The processes mentioned above convert liquid petroleum oils into gasoline and other products. The thermal conversion of hydrocarbon gases transforms gaseous hydrocarbons into gasoline. The following commercial applications of cracking are discussed below:

1. Conversion of liquid petroleum products into gasoline in the residuum process.

2. Conversion of liquid petroleum products into gasoline in the non-residuum process.
3. Conversion of liquid petroleum products into aromatic hydrocarbons.
4. Viscosity breaking of heavy viscous oils.
5. Reforming of naphthas or gasolines.
6. Conversion of hydrocarbon gases into gasoline.

Residuum Cracking Process

The residuum process is the most widely used application of cracking; it may be performed by any method. The non-catalytic, mixed-phase operation with recycling is the most important method of the commercial residuum process. Selective cracking in combination units, as a modern modification of the residuum process, is widely used in large refineries. Very promising results are obtained by the introduction of catalytic cracking in the residuum process.

Any petroleum product, including crudes, can be employed as a charging stock in the residuum pressure process. As has been explained above, in modern practice only clean distillate stocks are heavily cracked under comparatively severe conditions. Crudes and residues are subjected to a preliminary moderate cracking in viscosity breaking operations which give distilled stocks for final cracking, partially as a result of straight-run distillation and partially by light cracking of heavy hydrocarbons.

In addition to gasoline, gas and residuum, furnace oil can also be obtained at the sacrifice of the yield of gasoline. The furnace oil is a lighter fraction of recycle stock conforming to the specification of this product. Due to the flexibility of the operation, the yields of gasoline and furnace oil may be controlled according to the demand for both products.

The residues obtained in the residuum process have the properties described in Chapter 7. It would be of interest to notice that a few years ago the cracked residues contained an appreciable amount of free coke—about 1 per cent or more. The content of coke in cracked residues produced in modern units amounts usually to 0.1 per cent or less, due to considerable progress in the design of heaters, as well as to the introduction of the viscosity breaking operation. The residuum process is carried out with minimum (almost zero) coke formation.

The yield of gasoline in the residuum process is closely related to the properties of the residuum. As has been explained previously, the specific gravity of the residuum predetermines, to a certain extent, the relative amount of the condensed polycyclic aromatic hydrocarbons present in the residuum. The difference in the specific gravities or A.P.I. gravities of the original stock and residuum defines, to the same extent, the degree or intensity of the cracking. According to Nelson,³³ there is a linear relationship between the yields of 400°E.P. gasoline from gas oil or

fuel oil, Y , and the difference in the A.P.I. gravities of the charging stock and residuum, $C-R$, expressed by the following equation:

$$Y = 25 + 1.5(C-R) \quad (36)$$

It is assumed that gas, gasoline and residuum are the sole products of cracking, and that no other distillates are withdrawn from the unit. In practice the pressure distillate may have a higher end point than 400°F. It results in a correspondingly higher yield of pressure distillate and a lower yield of residuum. Equation (36) gives fairly satisfactory results, very close to the yields produced in commercial operation.

When furnace oil is withdrawn from the unit, it may be assumed that 1½ per cent of the furnace oil withdrawn corresponds to a decrease of one per cent in the yield of gasoline. In this operation the total yield of gasoline and furnace oil is higher at the expense of the yields of gas and residuum.

The relationship between the yield of gas, Z , and the difference in the A.P.I. gravities of the charging stock and residuum, $C-R$, also is linear and is expressed, according to Nelson, by the equation:

$$Z = 0.45(C-R) \quad (37)$$

However, the accuracy of this equation does not exceed 50 per cent.

Both equations are valid only for the mixed-phase process and are invalid for the vapor-phase and catalytic operations.

In the vapor-phase residuum process the yields of gasoline are lower at the expense of greater gas formation under more drastic cracking conditions. The temperature of the vapor-phase process is a fundamental factor predetermining the yields of gasoline. The vapor-phase processes, requiring rather moderate temperatures of about 575°C. (1067°F.), give high yields of gasoline close to those obtained in mixed-phase cracking.

As has been mentioned in one of the preceding sections, the catalytic residuum process in the presence of activated clay does not produce residuum in the customary meaning of this term. Thus, gasoline, catalytic gas oil and gas are the products of catalytic cracking, not including the coke, which is deposited on the catalyst and is burned out in the operation of regeneration. As can be seen from Tables 65 and 66, gas formation in catalytic cracking is much less than in thermal cracking.

Only distillates of a suitable boiling range may be treated in vapor-phase and catalytic cracking.

Non-Residuum Process

In the non-residuum process the cracked residues formed are decomposed completely to recycle stock and coke. As a result, only gas, gasoline and coke are produced in this process. Any method of cracking may be used in the non-residuum process. Non-catalytic mixed-phase operation with recycling and, during recent years, selective mixed-phase cracking are in wide use.

Gas oils and residues may be employed as charging stocks for the non-residuum process. Heavy crudes and residues are used more frequently due to the poor properties of cracked residues produced from these charging stocks.

As in the case of the residuum process, furnace oil can also be produced in the non-residuum process, in addition to gasoline, gas and coke.

Coke formation in the non-residuum process is closely connected with the specific gravity of charging stocks. The specific gravity of the petroleum products predetermines approximately the relative amount of polycyclic hydrocarbons which are predominant coke-forming constituents in cracking. On the other hand, there is a certain correlation between the yields of gasoline, Y , in the non-residuum process and the specific gravity of the charging stock, S , which Nelson³³ expresses by the following two equations:

$$Y = 331 - 300S \quad (38)$$

for gas oils and

$$Y = 303 - 250S \quad (39)$$

for fuel oils.

It is surprising that the yield of gasoline from fuel oil in the non-residuum process is greater than from gas oil at the same specific gravity. For instance, the yields when 0.9-specific gravity stocks are cracked in the non-residuum process are 78 per cent for fuel oil and only 61 per cent for gas oil. This may be explained by the difference in the fractional composition of fuel and gas oils. At the same specific gravity, the fuel oils contain a considerable percentage of low-boiling fractions which are cracked, with high yields of gasoline.

It is understood that the yields of gasoline are lower when furnace oil is withdrawn from the unit. According to Watson,⁵⁵ the effect of the withdrawal of furnace oil upon the yield of gasoline may be illustrated by the following data (Table 69).

The data of Table 69 show that a decrease of 1 per cent in the yield

Table 69. Yields from 25°A.P.I. Mid-Continent Reduced Crude in the Non-Residuum Process.

Product	Gasoline + Coke Operation	Gasoline + Furnace Oil + Coke Operation
Gasoline, 400°F. E.P. (% by vol.)	70	49
Furnace oil (% by vol.)	None	29
Coke (lbs. per bbl.)	65	47
Gas (cu. ft. per bbl.)	940	730

of gasoline corresponds to 1½ per cent of the furnace oil withdrawn, as in the residuum process. The formation of gas and coke is lower, when furnace oil is withdrawn, due to the lesser extent of cracking.

The yields of cracked gasoline in the non-residuum process are higher than in the residuum operation at the expense of complete cracking of the

residuum. It should be borne in mind that the yields of cracked residues of the same specific gravity are much greater for residual oils than for gas oils or distillates. Thus, the relative increase in gasoline yield in the non-residuum process in comparison with the residuum operation should be greater for residual oils than for distillates and gas oils. A very considerable gain in gasoline yield is obtained in non-residuum cracking of straight-run residues, as the data of Table 70 clearly show.

Table 70. Residuum and Non-Residuum Cracking of Reduced Crudes.

Product	Residuum Process	Non-Residuum Process	Increase in Yield in Non-Residuum Process (%)
25° A.P.I. Mid-Continent Reduced Crude			
Gasoline, 400°F. E.P. (%)	53.5	70.0	30
Residuum, 7° A.P.I. (%)	37.5	None	
Coke (lbs. per bbl.)	None	65	
20° A.P.I. M.C. and W. Texas Fuel Oil			
Gasoline (%)	44.3	62.0	40
P.D. Bottoms (%)	11.8	12.2	
Residuum, less than 10° A.P.I. (%)	38.4	None	
Coke (lbs. per bbl.)	0.3	75	

Thus, the increase in gasoline yield in the non-residuum process over that in the residuum operation is from 30 to 40 per cent, if straight-run residues or reduced crudes are cracked. The data of Table 70 correspond to very heavy cracked residues, produced in the residuum process, of 7-8° A.P.I. gravity. The increase in gasoline yield in the non-residuum process would be still greater, if the cracked residues had a higher A.P.I. gravity.

In the residuum cracking of gas oils the yield of cracked residues is comparatively small, usually in the neighborhood of 25 per cent of the fresh charge. Thus, the increase in the yield of gasoline in the non-residuum process for gas oils is much smaller, usually not exceeding 15-20 per cent. With respect to the yields of gasoline, the advantages of the non-residuum process are greater for the cracking of residual products.

The octane number of cracked gasoline in the non-residuum process is either equal to that in the residuum process or slightly lower.

The yield of coke in the non-residuum operation depends on the aromaticity or specific gravity of the charging stocks. The approximate yields of coke versus A.P.I. gravity are as follows:

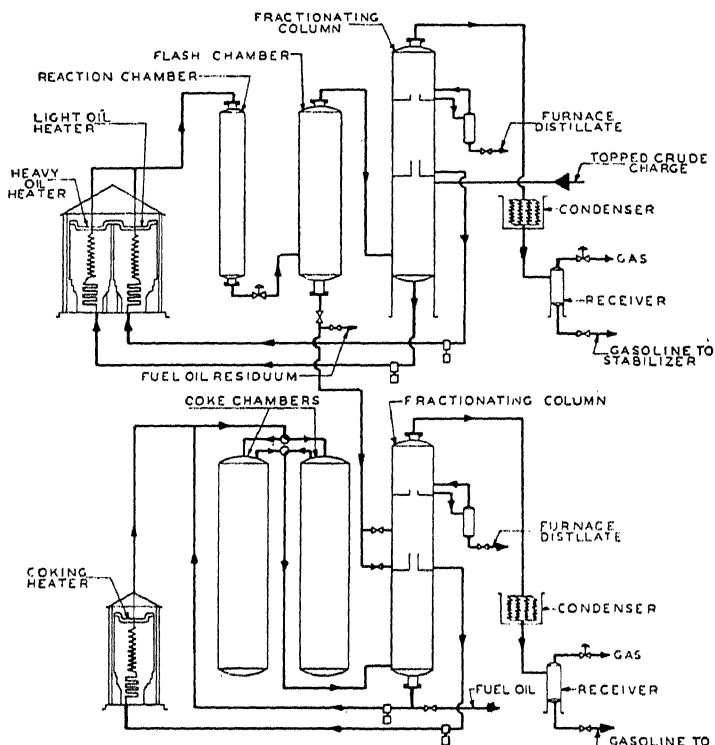
A.P.I. Gravity	Yield of Coke, Lbs. Per Barrel*
10	120
15	100
20	85
25	65
30	50

* These yields of coke correspond to the total conversion of the charging stock to gas, gasoline and coke without formation of other distillates.

As has been stated in a previous section, coke formation in the Houdry catalytic process takes place on the catalyst. The coke formed is burned

out in the regeneration operation and, therefore, is not obtained as a commercial product. Catalytic gas oil is obtained instead of cracked residuum.

The formation of coke in modern non-residuum cracking units takes place in two coking chambers operating alternately. As a result, the process is practically continuous. A comprehensive scheme of the selective non-residuum process described by Watson⁵⁵ is given in Figure 10.

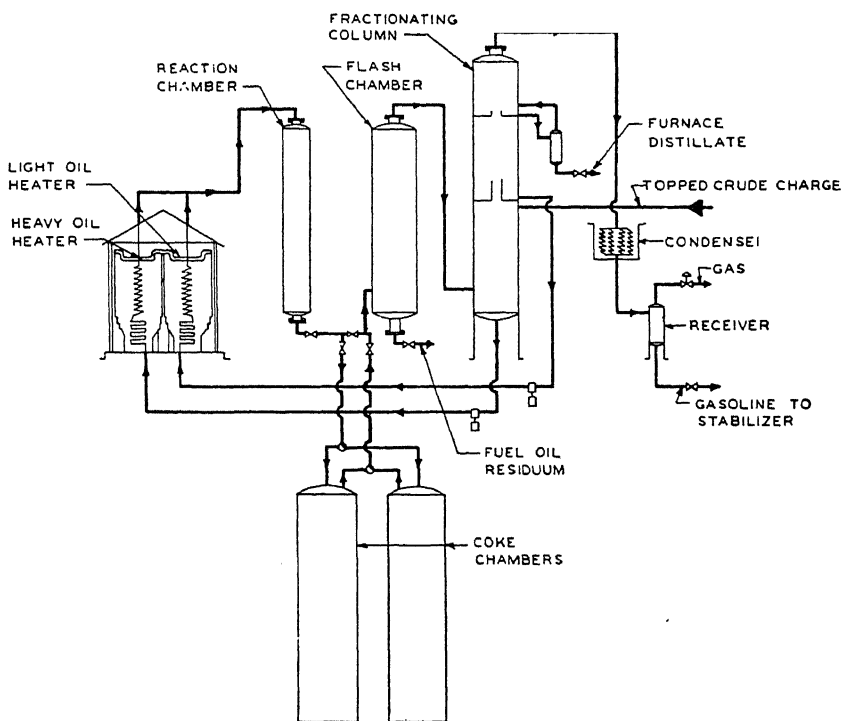


Courtesy "National Petroleum News"

FIGURE 10.—Flow Chart of Non-residuum Cracking.

After direct heat exchange in the fractionating column, the topped crude, blended with heavy recycle stock, is cracked in the first heavy oil heater under comparatively moderate temperature conditions. The lighter recycle stock (including furnace oil when gasoline only is manufactured) is cracked in the second light oil heater under more severe conditions. The residuum from a flash chamber is discharged to the second fractionating column where the low-boiling distillates are stripped out. The furnace-oil fraction obtained in this column may be returned as a charge for cracking. The residuum from the second fractionating column is pumped to the coking heater where the temperature of the residuum is

raised to 900-950°F. in the outlet. From the coking heater the residuum is conveyed to one of the coking chambers for final decomposition. The distillates formed in the coke chamber are returned to the second fractionating column as a recycle material for the coking operation. The coking chambers usually operate under a pressure of 100 to 150 pounds per square inch gauge. The operation time is from 24 to 48 hours.



Courtesy "National Petroleum News"

FIGURE 11.—Flow Chart of Non-residuum Cracking.

Various modifications of the scheme discussed above are possible. Figure 11 represents a certain simplification of the process described. The cracking residuum from the reaction chamber enters directly one of the coking chambers. Thus, the coking heater is eliminated. The distillates from the coking chamber are conveyed to the flash chamber for further separation of the fractions.

At the present time the non-residuum process is gaining in commercial importance due to the overproduction and low prices of heavy fuel oil.

Aromatization of Liquid Petroleum Products

The cracking of petroleum products at temperatures of 650°C. (1202°F.) and higher at atmospheric pressure leads to the formation

of highly aromatic products. The yields, however, are poor, and at present the process in question is of small commercial importance. The high-temperature aromatization of petroleum products was largely used during the World War for the production of benzene and toluene and is still used on a large scale in the U.S.S.R. for the same purpose.

The primary reactions in the aromatization of petroleum products are various processes of decomposition, including rupture of the rings of cyclic hydrocarbons. High gas formation is a result of these reactions. Olefins are largely yielded in the first stages of the process.

The formation of aromatic hydrocarbons of the benzene series in this process at 650°C. (1202°F.) and higher is mostly due to the secondary reactions of cyclization and condensation of olefins. It explains why the yields of benzene hydrocarbons under these conditions are almost independent of the nature of charging stocks, in contradistinction to the customary cracking practice at more moderate temperatures.

Cooke, Wagner and Swanson^{3a} give the following yields of products obtained by aromatization of a paraffinic gas oil of 34°A.P.I. gravity:

Aromatic gasoline, 31.2 A.P.I.	30 per cent
Tar	30 " "
Gas	40 " "

The aromatic gasoline consists mostly of aromatic hydrocarbons.

Kaplan and Forney^{24a} described the Forward process for producing aromatic gasolines (C. B. Forward, U.S.P. 2,007,087, 1935). The process is continuous and is performed at a temperature of about 1050°F. and a pressure of 225 pounds. The yield of synthetic crude from gas oil is close to 70 per cent. Gasoline constitutes about 50 per cent of the synthetic crude. The aromaticity of the gasoline is reported to be 85-91 per cent. The results are similar to those described by Cooke *et al.*

The temperature conditions of the processes described are not too severe and approach those of high-temperature vapor-phase cracking.

The process of aromatization, carried out at temperatures of 650-750°C. (1202-1382°F.), yields about 40-45 per cent of liquid aromatic products and 50-55 per cent of gas. The yield of coke, 5 per cent or more, depends upon the nature of the charge. As charging stock, any petroleum product, distilled or residual, can be processed at least in proper installations. The process is a once-through operation.

The gasoline fraction of the aromatic products formed, 400°E.P., contains approximately 60 per cent of aromatics and 30 per cent of olefins, if the temperature of the process is of about 650°C. (1202°F.). The aromaticity of the fraction is still higher at higher temperatures. The yield of the 400°E.P. fraction is about 30-35 per cent of the total amount of liquid aromatic products. Benzene, toluene, xylenes and naphthalene are produced from the lighter fractions. The maximum yields of benzene and toluene are approximately 6 per cent for each product, on the basis of the charge.

Still higher temperatures up to 800°C. (1472°F.) are employed, if not aromatic hydrocarbons but gases are manufactured in high-temperature cracking (Blau gas, Pintsch processes, etc.). As a result, the yield of gases increases up to 70 per cent by weight, and about 25 per cent of tar and 5 per cent of coke are formed. The composition of the gas produced will be given in Chapter 7.

High-temperature aromatization, as well as high-temperature gasification of petroleum products, is performed in tube heaters or in retorts. According to the extensive practice of Russian refineries, continuous operation in tube heaters gives unsatisfactory results due to very rapid wear of the tubes under high-temperature conditions. Tubes made of special alloys, however, may give much better performance. It is understood that only light distillates can be processed in tube heaters, whereas any distillates and residues are cracked in retorts, producing about the same yields of aromatic hydrocarbons.

The retorts used in the aromatization of petroleum products are made either of iron or of schamott. The ceramic retorts are preferred because of their long service which can last up to 5 years. The service of cast-iron retorts usually does not exceed 5 months.

If retorts of a small size are used, for instance about 5 feet long and 10-15 inches diameter, they are arranged in series in an oven and heated externally by burners, as in the gas works. Larger retorts, for instance about 20 feet long and 3-7 feet diameter, are heated periodically and internally by the combustion gases. After they have been heated to the required temperature of about 670°C. (1238°F.) or higher, the product to be cracked is introduced for decomposition. The process is continued until the temperature of the retorts decreases to a certain temperature in the neighborhood of 650°C. (1202°F.). The decomposition products are conducted to the collecting part of the installation. When the cycle is over, the vapors and gases remaining in the retorts are removed, and the retorts are heated again. The time of heating, as well as that of decomposition, is about 1 hour. Coke and soot deposited in the retorts are periodically burned out by air. The consumption of fuel for this process is high, amounting to 20 per cent of the charge.

A new method of aromatization of liquid petroleum products, "Sarmiza," being developed in Roumania,^{29b} uses three stages in the continuous process under atmospheric pressure. No catalysts are employed. The product evaporized is treated at 500°C. (932°F.) for cracking and producing olefins. In the second stage at 600°C. (1112°F.) the olefins are supposed to be transformed into cycloolefins which in turn are dehydrogenated to aromatics in the third stage at 720°C. (1328°F.). The following products are obtained from a kerosene of specific gravity 0.809:

Gasoline	64.4	%	by weight
Other liquid products	21.3	"	"
Gas	10.0	"	"
Losses	4.3	"	"

The gasoline produced has the following properties:

Specific gravity	0.838
Engler distillation (°C.)	58-167
Aromatics (%)	85.3
Olefins (%)	2.0
Paraffins and Naphthenes (%)	12.7
Octane number, motor method	92

The exceptionally high yields of gasoline reported should be noticed.

Viscosity Breaking

Viscous heavy crudes and residues are converted into fuel oils of low viscosity in the viscosity breaking process. This is carried out in the liquid phase in a once-through operation under mild temperature-time conditions. As has been previously pointed out, viscosity breaking of heavy residues takes place in the first stages of cracking when the most unstable long paraffinic side chains of aromatic and hydroaromatic hydrocarbons are split, with formation of intermediate cracked fractions. The splitting is accompanied by a strong decrease in viscosity due to decomposition of the most viscous cyclic hydrocarbons having long paraffinic side chains. The data of Table 71 show the gradual decrease in viscosity of a very heavy and viscous Kaluga crude in the viscosity breaking operation.

The formation of gasoline is very small under the conditions given above, resulting in a drop in flash point. The viscosity at 68°F. decreased a hundred times after viscosity breaking in the last experiments of Table 71.

Table 71. Viscosity Breaking of Kaluga Crude at 415°C. (779°F.), 10 Atm. Pressure.

Time of Cracking (min.)	Sp. Gr. at 15°C.	-----Viscosity-----		Flash (°F.)	Coke (%)	Gas and Loss on Charge
		at 68°F.	at 122°F.			
None	0.957	1850 S. Fur.	905 Sayb	277	0.09*	None
13	0.946	1250 Sayb.	219 "	147	0.11	2.0
22	0.938	450 "	111 "	122	0.09	2.1
32	0.935	265 "		106	0.29	2.6

* The 0.09 per cent coke which was found in the original crude is undoubtedly due to mineral admixtures present in the crude.

The commercial viscosity breaking of heavy viscous residues is performed at a temperature of about 460°C. (860°F.) and under the moderate pressure of 200 to 500 pounds per square inch gauge.

Frequently viscosity breaking is performed, not as a separate operation, but as a link in the chain of operation of combination units. The topped residues, usually mixed with heavy recycle stock, are cracked in the viscosity breaking heater of the combination unit under moderate conditions of temperature up to 480°C. (896°F.). The main purpose of this operation is distillation of the topped crude for producing the distillates to be cracked under selective conditions of temperature, time and pressure. As a result of the viscosity breaking operation, the viscosity of the residuum is considerably reduced in comparison with that of the

straight-run distillation of the same topped crude. The operation of the combination units has been described in a special section.

Viscosity breaking also may be performed catalytically in the Houdry process.²³ The temperature range of catalytic viscosity breaking is between 371 and 481°C. (700 and 900°F.) and preferably between 421 and 455°C. (790 and 850°F.).²¹ Table 72 gives some data on catalytic viscosity breaking.

Table 72. Catalytic Viscosity Breaking Heavy Crude Residues.

Source	West Texas- New Mexico Residuuum	Coastal and East Texas Residuuum
Residue charge		
Gravity (A.P.I.)	8.5	12.6
Viscosity (Saybolt, 210°F.)		734
Sediment (%)	0.3	0.01
Gas oil* (% of charge)	3	5
Fuel oil product		
Gravity (A.P.I.)	11.6	14.5
Viscosity (Saybolt, 122°F.)	145	159
Pour point (°F.)	30	25
Flash point (°F.)	150	154
Sediment	0.4	0.08
Volume (% on residue charged)	98.5	102
Naphtha (% by vol. on residue charge)	1.0	2.1
Gas (% by wt. on residue charge)	3.5	1.5
Catalyst deposit (% by wt. on residue charged)	1.8	0.4

* Gas oil used for washing in process and appearing in final product.

The pour points of residues also may be lowered in the process of viscosity breaking but the effect of this process on the pour points is much smaller. It should be borne in mind that the high pour point of fuels is due to the presence of paraffin wax which produces its pour increasing effect even in comparatively small concentrations.

Reforming

Reforming is a cracking process for converting low octane number naphthas or gasolines into high octane number products. The process can be carried out in mixed phase under high pressure and in vapor phase, both non-catalytically and catalytically. Commercial operation utilizes the high-pressure mixed-phase process, if the last term may be applied to reforming. As a matter of fact, reforming of gasolines takes place completely in vapor phase. Reforming in vapor phase under low pressures is not used commercially due to lower yields and instability of the product reformed in the vapor phase. The use of certain catalysts in reforming seems to be very promising.

Reforming is carried out under rather severe temperature conditions. The temperature is from 500 to 560°C. (932 to 1040°F.) and the pressure from 250 to 1000 pounds per square inch gauge. The temperature most widely used in reforming is about 530°C. (986°F.). The cracking time is about 10-20 seconds at 1000°F. Due to the high temperatures used in reforming, and the short time of cracking, reaction chambers are usually not employed. In catalytic reforming (the Houdry process) the temperature is somewhat lower, from 455 to 510°C. (850 to 950°F.) and preferably from 468 to 490°C. (875 to 925°F.).²¹

The equipment employed in Houdry reforming duplicates that used in the Houdry cracking process.^{36a} Thus a conventional Houdry plant may be used for cracking as well as for reforming. When reforming naphthas, the throughput rate is almost doubled as compared with cracking gas oils (approximately 2 volumes of naphtha per hour per one volume of catalyst versus 1 volume of gas oil). The time of operation is 10 minutes or more. Houdry reforming is accompanied by partial desulphurization.

Catalytic reforming in the presence of bauxite has been described by Foster.^{13a} This is performed at 524°C. (975°F.) and under 30-55 pounds' pressure with flow rates of 265 to 420 barrels per ton of bauxite per day. In addition, the process removes up to 75 per cent of the sulphur present in gasolines. The operation time of the catalyst is about twenty-four hours. Regeneration is reported to be rather simple. Still better results may be obtained when a synthetic catalyst is used instead of bauxite. High yields of 80 octane number reformed gasoline are reported in the presence of synthetic catalysts, such as chromic oxide. Catalytic reforming simultaneously reduces appreciably the content of sulphur in reformed gasolines as compared with the original naphthas. This process at more moderate temperatures may be adapted especially to desulphurization, as will be discussed in Chapter 6. Schulze [U.S.P. 2,167,602 (1939)], gives the following conditions of reforming in the presence of bauxite:

Temperature	477-565°C. (900-1050°F.)
Pressure	atm.-100 lbs./sq. inch.
Rate	1-10 liq. vol. of gasoline per vol. of bauxite per hour.

Recycling is not necessary in reforming, since the coke-forming ability of naphthas is insignificant, and a high conversion per pass can be obtained without coke formation. In addition to this, the octane numbers of reformed gasolines are greater when a high conversion in a once-through operation is obtained. Thus, reforming is mostly a once-through process, and recycling with a small recycling ratio is used in few reforming units.

As charging stocks, gasolines and mostly heavy naphthas are reformed. Frequently, heavy naphthas are blended with light kerosenes. Straight-run paraffinic naphthas and cracked naphthas of low octane number are the usual charging stocks.

The yields of reformed gasoline depend on the cracking conditions. On the other hand, they depend upon the octane number of the reformed gasoline, as will be shown later. Yields of thermally reformed gasoline vary between 70 and 90 per cent, if the octane number of the reformed gasoline is close to 70. In addition to gas, a small amount of residuum is produced in reforming, due to the condensation reactions. The average balance of the reforming products may be summarized as follows:

Reformed gasoline	75 per cent
Gas	18 " "
Residuum	7 " "

The lower the octane number of the naphtha to be reformed, the smaller the yield of 70 octane number gasoline. In catalytic reforming the yields of reformed gasoline are appreciably higher than in the non-catalytic process. The yield of catalytically reformed exceeds that of thermally reformed product usually by 5-10 per cent for an equal improvement in octane number.

The yields and properties of reformed gasolines in Houdry reforming are summarized in Table 72a.

Table 72a. Catalytic Reforming Naphthas to Produce Motor Fuel.

	Coastal Naphtha	E. Texas Naphtha	W. Texas Naphtha
Rate of charge to catalyst, liquid vol. of naphtha per vol. of catalyst	2.25	2.0	3.8
Charge:			
Gravity A.P.I.	46.8	50.4	59.2
A.S.T.M. distillation (°F.)			
I.B.P.	154	245	110
50%	334	308	250
E.P.	464	413	414
Sulphur (%)	0.03	0.02	0.21
O.N., S.F.R. M.M.	57.2	43.4	53.2
Yields:			
Total liquids (% by vol.)	92.5	94.1	95.1
Gasoline (% by vol.)	83.4	90.4	93.6
Reformed Gasoline:			
Gravity A.P.I.	57.8	57.5	63.0
A.S.T.M. distillation (°F.)			
I.B.P.	104	94	96
50%	256	284	227
E.P.	392	390	383
Sulphur (%)	0.01	0.01	0.01
O.N., S.F.R. M.M.	76.5	61.8	63.5
Copper dish gum, mgr/100 cc.	1	1	1
Induction period (hours)	10	10	10

The yield and properties of reformed gasoline produced from a Michigan straight-run gasoline in the presence of bauxite are as follows (Schulze, *loc. cit.*).

Yield, % by vol.	97	
Gas formed	260	cu. feet/bbl.
Octane No., S.F.R. Motor	51.7	(36.8 str. run)
Same with 3 cc. tetraethyl lead	74.7	(58.6 str. run)
Sulphur content	0.004	(0.050 str. run)

It is of interest that the gas contains 82 per cent hydrogen, indicating a great extent of dehydrogenation reactions in reforming.

Reforming reactions are mostly dehydrogenation, decomposition of paraffin hydrocarbons to low molecular weight paraffins and olefins and various aromatization reactions. Paraffins and olefins of low molecular weight are responsible for the gas formation. Aromatic hydrocarbons are formed as a result of the dehydrogenation of alkylated naphthenes of the virgin naphtha as well as of various secondary reactions involving olefins, which have been discussed in Chapter 1. Due to a small content of poly-cyclic aromatics and naphthenes in naphthas, the reactions of condensa-

tion do not play any important part in reforming, and the yield of high molecular condensed hydrocarbons is small.

As a result of reforming, the fractional and chemical composition of reformed naphthas is changed. Owing to the formation of low molecular weight hydrocarbons, the reformed gasolines are richer in low-boiling fractions than are the virgin naphthas. The change in chemical composition is still more significant. Whereas the virgin low octane number gasolines consist predominantly of paraffins and naphthenes, the reformed gasolines contain paraffins, olefins, naphthenes and aromatics. The proportion of paraffins in reformed gasolines is much smaller than in virgin naphthas.

Increase in the octane number of reformed gasolines is largely due to change in the chemical composition. Also, formation of low-boiling fractions of comparatively high octane number should not be overlooked. Table 73 gives the data of Turner and Le Roi⁴⁹ on the increase in octane numbers on reforming.

Table 73. Octane Numbers of Virgin Naphthas and Reformed Gasolines: C.F.R. Motor Method.

A.P.I. Gravity of Virgin Naphtha	Octane No. of Virgin Naphtha	Coil Outlet Temp. °F	Equivalent Seconds at 900°F.	Octane No. of Reformed Gasoline	Increase In O.N.
50.3	35.7	1000	499	70.4	34.7
51.2	34.0	1020	348	63.4	29.4
50.7	36.2	980	235	63.4	27.2
	33.5	975	147	56.1	22.6
45.2	55.9	1015	645	70.7	14.8

These data clearly show that the effect of reforming (increase in octane number) depends upon the temperature-time factor of the process. In Table 73 the equivalent time at 900°F. is a measure of the temperature-time factor. On the other hand, the effect of reforming for a high octane number naphtha (55.9) is much lower than in the case of low octane number naphthas (34-36.2), other conditions being the same. The proportion of low octane number paraffins is much smaller in high octane number naphthas, and the effect of reforming should be correspondingly small.

The close connection between the yields and octane numbers of reformed gasolines is another expression for the effect of the temperature-time factor. It is self-evident that the yields of reformed gasoline decrease with increasing temperature-time factor. Le Roi and Ferguson²⁸ showed that improvement in octane number is closely connected with the yield of reformed gasoline or with the degradation of the original naphtha to gas and tar. The octane number of reformed gasolines may be increased to 85-90 and even higher at the sacrifice of yields. According to Le Roi and Ferguson, the most favorable results of reforming are obtained in a once-through operation without reaction chamber. The use of soakers slightly increases the percentage of degradation and the recycling operation gives the maximum percentage of degradation for the same improvement in octane number.

Reforming is widely used in petroleum refining. The reforming cost is

comparatively low due to the once-through operation and does not exceed 12¢ per barrel of charging stock.

As has been mentioned above, the reforming of low-octane naphthas can produce reformed gasolines of octane number 70 and higher. However, the combination of reforming and ethylization usually gives better commercial results than reforming alone. For this reason reforming is frequently performed to an octane number lower than 70. The subsequent ethylization increases the octane number to the required level. The economics of reforming and ethylizing have been discussed by Keith, Carey and Ward.^{24b} Reforming and subsequent ethylizing of low-octane number straight-run gasolines of 45 octane number to produce 70-octane gasoline is much more profitable than ethylizing alone. However, the differential between reforming plus ethylizing and ethylizing only, decreases with increase in octane of the original gasoline. There is a very small margin between the cost of 70-octane gasoline ethylized only, and reformed plus ethylized, when the octane number of the original gasoline is about 55.

Tongberg *et al.*^{47a} pointed out that the knocking properties of low-octane number straight-run gasolines depend mainly upon the presence of normal paraffins from hexane to nonane. A Bradford straight-run gasoline of octane number 42 was fractionated in a column having 75 theoretical plates with the reflux ratio 40:1. The fractions boiling in the range 147°-160°F., 200-210°F., 253-269°F., and 293-309°F., corresponding to the normal paraffins, had octane numbers from 0 to 37, while other fractions were of much higher octane number, from 44 to 80. The total amount of the knocking fractions was 24.7 per cent. These results may indicate a possible future trend in reforming. The reforming of selected, badly knocking fractions produced by close fractionation, and the blending of reformed and straight-run fractions, may give higher yields and better octane rating and stability of gasoline as compared with the conventional method of reforming.

Reforming of low-octane number naphthas may be carried out in the presence of olefin-containing gases, for instance, Wagner, C.R., U.S.P. 2,157,224 (1939); Mashwitz, P.A., 2,165,804 (1939). As a result, reforming is accompanied by polymerization or thermal conversion of olefinic gases. The temperature of the process is in the range of conventional reforming and the pressure is from 500 to 3000 lbs./sq. inch, which conditions may ensure simultaneous reforming and polymerization. There are no data available on the yields and properties of gasolines reformed by the process described.

Thermal Conversion of Gases

As has been stated in Chapter 1, there is a significant difference between the polymerization and the thermal conversion of hydrocarbon gases. The first process is the polymerization of olefins to high molecular olefins and naphthenes, accompanied by some side reactions, under mild conditions of temperature and in the presence of various catalysts. The process is

predominantly synthetic without appreciable occurrence of decomposition reactions. Various processes of polymerization have been described in Chapter 1. Only thermal conversion of hydrocarbon gases is discussed in this section.

The cracking or thermal conversion of gases is the high-temperature process embracing the same reactions of decomposition, polymerization and condensation which take place in ordinary cracking of liquid petroleum products. The only significant difference between the thermal conversion of gases and of liquid products is the low molecular weight of gaseous hydrocarbons. As a result, the reactions of polymerization and condensation leading to the formation of gasolines are of primary importance in the thermal conversion of gases. The decomposition reactions of gaseous paraffins, yielding olefins, are only a preliminary stage, followed by polymerization and condensation of the olefins formed to the heavier hydrocarbons of gasolines.

In order to understand better the temperature-pressure conditions of thermal conversion of gases, the processes of decomposition of paraffins and polymerization of olefins at high temperatures should be considered separately.

The extent of the decomposition of ethane and propane to olefins in a KA2S coil under atmospheric pressure *versus* temperature and time was studied by Sullivan, Ruthruff and Kuentzel.⁴⁴ Some of the data obtained by these authors are given in Table 74.

Table 74. Conversion of Paraffins to Olefins vs. Temperature and Time.

Temperature		Reaction Time (sec.)	Conversion to Olefins (% by vol.)
°C.	°F.		
Ethane			
782	1440	1.0	45
782	1440	2.0	51
816	1500	0.5	50
816	1500	1.5	66
843	1550	0.5	70
Propane			
677	1250	1.0	14
677	1250	2.0	20
704	1300	1.0	30
766	1410	0.5	40
766	1410	1.0	59
793	1460	0.5	57
793	1460	1.0	74
816	1500	0.5	73
816	1500	1.0	76

Butanes are converted into olefins under somewhat milder conditions of temperature and time than propane. The decomposition stage, taking place at very high temperatures, lasts a very short time, and is followed by secondary reactions of the olefins formed. As has been stated in Chapter 1, the reactions of olefins at high temperatures lead to polymerization, formation of aromatics, and condensation.

With respect to the yields of olefins, reactions of dehydrogenation

are preferable to those of decomposition, as the former give much higher yields of olefins. Unfortunately the decomposition reactions of paraffins are predominant, and the reactions of dehydrogenation under high temperature conditions, take place only to a small extent, as has been described in Chapter 1. However, in the presence of certain catalysts, such as alumina and chromic oxide, the dehydrogenation of paraffins may be performed very efficiently. A wide use of dehydrogenation catalysts in the first stage of the thermal conversion of gases seems to be a logical development of the process in question. The catalytic dehydrogenation of butanes has been described in Chapter 1.

The polymerization of ethene and propene to hydrocarbons of gasoline boiling range at high temperatures is comprehensively illustrated by the data of Sullivan *et al.* Some of these data are included in Table 75.

Table 75. Polymerization of Olefins vs. Temperature and Time.

Temperature °C. °F.		Pressure (lbs./sq. in.)	Time of Reaction (min.)	Conversion to Polymers (% by wt.) of Ethene of Propene	
399	750	500	10	4	2
399	750	1000	10	14	4
399	750	1000	30	49	13
399	750	3000	10	52	24
399	750	3000	20	73	54
454	850	500	10	65 (?)	45 (Extrapol)
454	850	1000	10	54	50 (Extrapol)
454	850	1000	20	65	57
454	850	3000	10	76	68

The comparison of Tables 74 and 75 illustrates very clearly the difference between the decomposition and polymerization stages. The temperature range of the decomposition is much higher than that of the polymerization. As can be foreseen, the pressure has a very strong effect upon the polymerization. It is of interest to note that thermally ethene is more polymerizable than propene, while in catalytic polymerization ethene is much more inert than high molecular weight olefins.

As will be seen from the data of Tables 74 and 75, the temperature and pressure conditions of thermal conversion of gases should differ very substantially from those of cracking of liquid petroleum products. The low molecular weight paraffins, including butanes, are much more stable than the high molecular weight hydrocarbons of liquid charging stocks. Thus, the temperature of cracking of gaseous hydrocarbons should be higher than in the case of liquid petroleum products. Practically, only propane and butane can be cracked and processed in modern commercial gas converting units. Ethane, and particularly methane, are too stable thermally to be cracked in any modern gas converting installations. Theoretically the process of the decomposition of paraffins should be performed at low pressures.

On the other hand, more moderate temperatures and higher pressures should be used for the polymerization of the olefins formed. The process of thermal conversion may also take place under low pressure and high

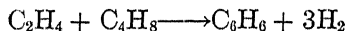
temperature, producing mostly aromatic hydrocarbons as a result of condensation and aromatization reactions at high temperatures. As has been shown in Chapter 1, the condensation processes of unsaturates into cyclic hydrocarbons have negative values of free energy at low pressures.

The conditions of the decomposition and polymerization reactions of hydrocarbon gases may be summarized as follows:

1. Cracking or decomposition of paraffins (propane and butanes and partially ethane) takes place at temperatures of 550°C. (1022°F.) or higher under low pressures.

2. Polymerization of olefins requires lower temperatures [about 500-550°C. (932-1022°F.)] and high pressures. Both conditions favor the polymerization of olefins as well as possible alkylation of paraffins with olefins. Polyolefins and naphthenes are formed as a result of polymerization, and paraffins as a result of alkylation. It is understood that the latter process takes place only under very high pressures of 3000 pounds per square inch gauge and higher, as has been stated in Chapter 1. Paraffins can be formed as a result of other secondary reactions also. A more advanced conversion yields gasolines which are more or less aromatic. Polymerization under these conditions produces gasolines consisting of various hydrocarbons, including paraffins, olefins, naphthenes and aromatics.

3. Condensation of olefins may take place at high temperatures above 600°C. (1112°F.) and at low pressures. Under these conditions principally the condensation reactions of olefins, with formation of aromatics, take place readily, as for instance:



and other reactions of this type, that have been described in Chapter 1. As a result, highly aromatic gasolines and other aromatic products are formed, in contradistinction to the polymerization process.

Since methane and ethane are not converted in modern processes, the lean natural gases should be given a preliminary treatment for the concentration of propane and butanes. Refinery gases with a small content of C₃ and C₄ hydrocarbons also should be treated. Otherwise, handling large quantities of non-reactive gases would affect the yields of the products of conversion and increase the operating expenses. The concentration of C₃ and C₄ hydrocarbons may be performed either by absorption or by compression. Both methods, followed by fractionation under proper conditions of temperature and pressure, separate methane and ethane very efficiently, increasing the concentration of C₃ and C₄ hydrocarbons to 80-90 per cent.

Conversion of Gases in Two Stages

In the case of paraffinic gases, the two-stage process seems to be logical. The two- and multi-stage conversion of hydrocarbon gases was developed by the Pure Oil Company and Alco Products, Inc. In the first

stage, paraffin hydrocarbons may be decomposed and dehydrogenated at high temperatures of 600-700°C. (1112-1292°F.) forming olefins and low molecular weight paraffins. According to Cooke, Swanson and Wagner,³ the temperature of this stage may be as high as 705°C. (1300°F.) or higher. The pressure should be moderate or low due to the fact that decomposition reactions predominate.

The second stage of the thermal conversion of gases may be performed either at comparatively moderate temperatures and high pressures or at high temperatures and low pressures, as has been stated in the previous section. It can be directly applied to refinery gases containing olefins in a proportion of 20 per cent or more. For these gases the first stage of conversion, the decomposition and dehydrogenation of paraffins, is eliminated, and the olefinic gases are treated directly under the conditions of the second stage.

According to Cooke *et al.*, moderate temperature conversion is performed at a temperature of 482-538°C. (900-1000°F.) and at a pressure of 600 to 800 pounds per square inch gauge. The data on the process under these conditions are given in Table 76. A cracked gas from Gyro vapor-phase cracking was treated. The octane numbers of the gasolines produced under the above conditions are between 75 and 78 by the Motor Method.

Table 76. Conversion of Olefinic Gas.

Charging stock (including recycle)		
Specific gravity (air = 1)	1.51	
Unsaturation (mol. %)	49.4	
Recycle ratio	1.75	
Yields of products		
Gasoline, 398°F. E.P., per 1000 cu. ft. of fresh charge	8.8	Gal
Fuel oil (A.P.I. 8.0°)	3.0	"
Total of liquids	11.8	"
Gas after conversion, specific gravity	1.01	
Unsaturation (mol. %)	22.0	

The thermal conversion of olefinic gases at high temperatures and low pressures takes place at 621-705°C. (1150-1300°F.) and at a pressure of the order of 50 to 75 pounds per square inch gauge. As has been stated above, this process yields highly aromatic gasolines and other products. Cooke *et al.* reported the results on the thermal conversion of absorber gas of specific gravity 0.79 (air = 1) containing 39.4 per cent of olefins, mostly ethene. The conditions of the process were: temperature 1275°F. and pressure 60 pounds. The process yielded in a once-through operation 1.75 gallons of liquid products of 21.6°A.P.I. per 1000 cubic feet. With recycling, the yield can be increased to 3½-4 gallons per 1000 cubic feet. Under the same conditions, stabilizer overhead of specific gravity 1.352 yields in a once-through operation 9.8 gallons of liquid products of 26.4°A.P.I. per 1000 cubic feet of gas. The yield in a recycle operation would be approximately 11.0 gallons. The percentage of 350°F. E.P. gasoline in the liquid products is about 70. The gasolines obtained in

this process are almost entirely aromatic, of A.P.I. gravity 31-33° and of octane number 85-105.

An illustration of the yields in the two-stage operation is given in Table 77. Natural gas was used as a charging stock.

Table 77. Conversion of Natural Gas.

Charging stock	
Specific gravity (Air = 1)	0.815
Methane (mol. %)	70.5
Ethane	12.7
Propane	10.3
Butanes and heavier	6.5
Gas after first stage	
Specific gravity	0.695
Hydrogen (mol. %)	11.5
Methane	62.5
Ethane	5.1
Ethene	15.7
Propane	1.2
Propene	2.5
C ₄ and heavier	1.5
Liquid made	
First stage (gal. per 1000 cu. ft. of charge)	0.42
Second stage	2.38
Total	2.80
Gas after second stage	
Specific gravity	0.59
(cu. ft. per cu. foot of gas charged)	0.91

The yield of liquid products should be considered as fairly high, taking into consideration a small percentage of propane and butanes convertible into olefins. As will be seen from the figures of Table 77, propane and butanes of the natural gas were almost completely decomposed in the first stage of the process. Also, partial dehydrogenation of ethane is probable.

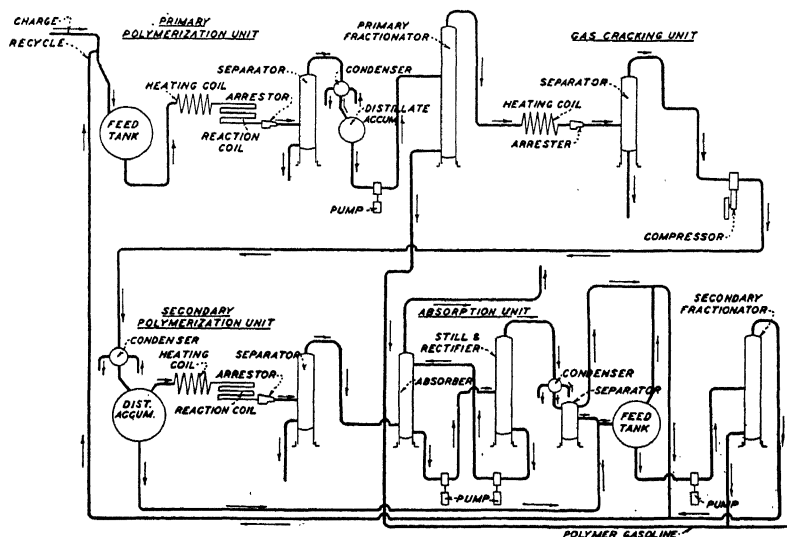
Figure 12 represents the scheme of one of the Pure Oil Company's gas conversion processes in three stages. A refinery gas is polymerized in the first coil (primary polymerization). The unreacted paraffinic hydrocarbons are cracked in the second coil (gas cracking) and the olefins formed are polymerized in the second polymerization coil. The gases from the coils are effectively quenched in arresters by recycled distillates.

The thermal cracking of paraffinic gases in the first stage may be combined with catalytic polymerization in the second stage. Mack^{20a} described a plant converting butanes into polymerized gasoline. Butane is thermally processed in the first stage to produce olefins. The exit gases from the cracking furnace have the following composition:

Hydrogen	15 mol. %	Propane	15.17 %
Methane	4.48 "	Butenes	0.82 "
Ethene	0.05 "	Butanes	46.00 "
Ethane	5.53 "	Pentanes and Heavier	0.41 "
Propene	11.36 "		

A small quantity of synthetic gasoline is also produced in the first

stage. The content of olefins in the exit gases is too small for catalytic polymerization (Chapter 2). Thus the gases are absorbed by oil to separate ethane and lighter hydrocarbons. The charge to the polymerizing stage, consisting mainly of butanes, butenes, propane and propene, contains about 24 per cent olefins to be catalytically polymerized, as has been described in Chapter 2.



Courtesy "National Petroleum News"

FIGURE 12.—Pure-Alco Gas Conversion Unit.

Conversion of Gases in One Stage

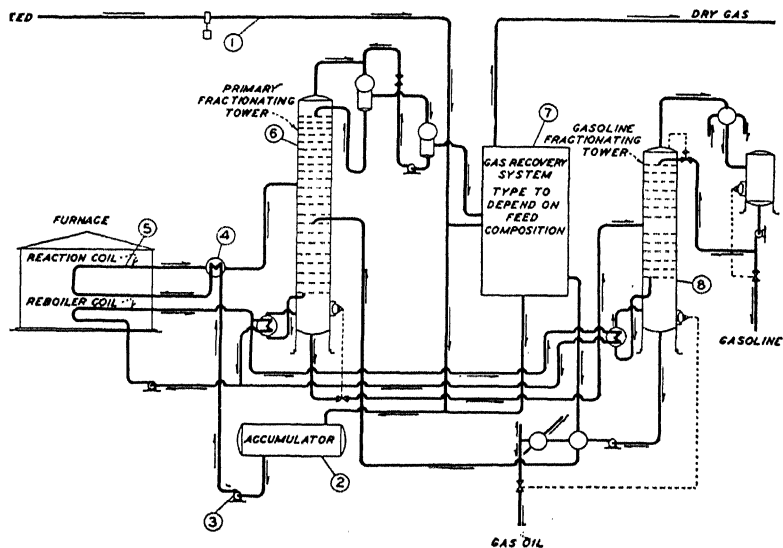
The thermal conversion of paraffinic, as well as olefinic, gases may be accomplished in one stage. At first glance it seems contradictory to theory that decomposition and dehydrogenation of gaseous paraffins and polymerization of the olefins formed can be carried out under the same temperature and pressure conditions. It should be emphasized, however, that the reactions of decomposition are practically irreversible, particularly under high pressures. The olefins formed as a result of decomposition and dehydrogenation take almost no part in the equilibrium with the virgin paraffins because of their polymerization and other secondary reactions. Even dehydrogenation of paraffins under high pressures, accompanied by polymerization, is irreversible. Thus, the decomposition of paraffins may take place either at low or at high pressures.

Tropsch, Thomas and Egloff⁴⁸ investigated the effect of pressure on the thermal conversion of gaseous paraffins, and found that a natural gas fraction at 550°C. (1022°F.), at the same conversion per pass, gave higher yields of liquid products with increasing pressure from 250 to 1000 pounds per square inch gauge, but correspondingly lower yields of

gaseous olefins. Thus, the pressure affected the polymerization and condensation processes more than it did the decomposition reactions.

The thermal conversion of gases in one stage has been developed as the Unitary Gas Conversion Process by the Phillips Petroleum Company, the Standard Oil Company of Indiana, the Standard Oil Company of New Jersey, the Texas Company, and the Kellogg Company.

The temperature employed in the Unitary Process is from 500 to 600°C. (932-1112°F.) and the pressure from 800 to 3000 pounds per



Courtesy "National Petroleum News"

FIGURE 13.—Flow Chart of the Unitary Process.

square inch gauge. The lower temperatures may be used for gases of high olefin content. The high pressure conditions are favorable to the polymerization of olefins. On the other hand, the temperature is sufficiently high to produce partial decomposition of propane and butanes. The olefins formed as a result of the decomposition are polymerized in the further stages of the process under the high pressures used. The scheme of the Unitary process is given in Figure 13, which seems to be self-explanatory.

Some data on the yields of liquid products in the Unitary Process are given in Table 78, according to the articles of Keith and Ward²⁵ and Ward.⁵² Data on the operation of the Unitary process plant at the Atlantic Refinery give the yield as 3.5 gallons per 1000 cubic feet of gas charged. The feed consists of 2.6 per cent of methane, 19.9 per cent of C₂, 61.6 per cent of C₃ and 15.9 per cent of C₄ hydrocarbons.⁵⁷ The octane numbers of the gasoline produced in the Unitary Process are close to 80 by the Motor Method.

Table 78. Conversion of Refinery Gases in One-Stage Process.

Feed Analysis			
Ethane (% by vol.)	3.0	12.2	6.8
Propane	83.0	46.3	49.6
Butanes	7.2	4.2	6.2
Ethene	0.7	3.4	1.9
Propene	3.9	29.6	30.5
Butenes	0.8	4.3	4.8
Temperature (°F.)	1100	1000	1000
Pressure (lbs./sq. in.)	2200	800	1200
Total yield of liquids (% by wt.)	56.0	67.9	69.0
Yield of 392°F. E.P. Gasoline (% by wt.)	52.1		
Gals. of liquids/1000 cu. ft. of charge	11.7	12.78	13.1

Wilson⁵⁸ has given a series of data on the commercial thermal conversion of paraffin hydrocarbons in the Unitary process. Butanes and propane can be processed at temperatures of about 555°C. (1030°F.). The greater thermal stability of propane compared with normal butane requires almost four times as large a soaking time and a furnace soaking volume. The following data illustrate the results of thermal conversion of propane and normal butane (Table 79).

Table 79. Thermal Conversion of Propane and Normal Butane.

	Propane	Normal Butane
Crack-per-pass (wt. %)*	5	8
Temperature (°F.)	1030	1030
Pressure (lbs./sq. in.)	1600	1600
Feed quantity (lbs.)	100	100
10 lb. R.V.P. Poly. liquid (lbs.)	51.7	67.6
Ultimate yield (wt. %)	51.7	67.6
Feed quantity (gals.)	23.5	20.5
10 lb. R.V.P. Poly. liquid (gals.)	8.5	11.0
Ultimate yield (volume %)	36.2	53.7
Furnace soaking (volume cu. ft.)	5.21	1.36

* Per cent by weight of 10 lbs. Reid V.P. liquid polymers with respect to the furnace charge.

As in the case of the cracking of liquid products, thermal conversion of saturated gaseous hydrocarbons may be carried out in a once-through operation only to a comparatively moderate extent. If the crack-per-pass is too great, the final yields of gasoline decrease and those of high-boiling condensation products increase. Tables 80 and 81 give data on the yields of gasoline and heavy residuum *versus* crack-per-pass.

Table 80. Yields of Gasoline from Propane and Butane Versus Crack-per-Pass.

Propane			
Crack-per-pass (wt. %)	5	7	9
Ultimate yield of 10-lb. R.V.P. polymer (wt. %)	51.7	50.0	48.2
Normal Butane			
Crack-per-pass (wt. %)	8	12	16
Ultimate yield of 10-lb. R.V.P. polymer (wt. %)	67.6	61.4	55.2

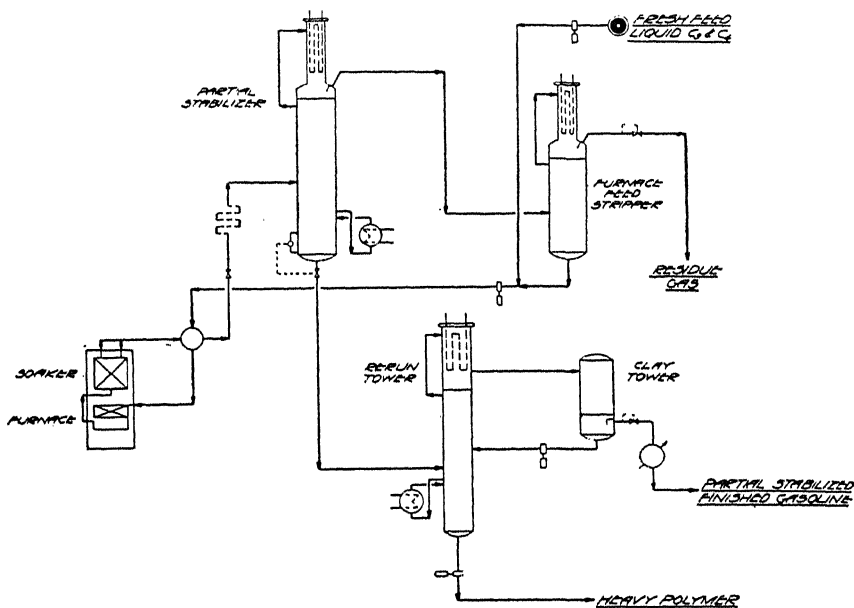
Table 81. Yields of Heavy Residuum* vs. Crack-per-Pass.

Crack-per-pass (wt. %)	4	6	8	10	12	14	16
Heavy polymer (wt. %)	0.3	2.1	4.1	6.0	8.0	9.9	11.9

* Fraction boiling above 400°F.

The scheme of a small unit for the conversion of butanes is given in Figure 14. The capacity of the unit is 40,000 gallons of butanes per day. The charge, combined with the recycle stock, is pumped to the furnace

containing a separate soaking coil. A rough separation of synthetic hydrocarbons from unreacted butanes and decomposition gases takes place in the first column. In the stripper the residual gas is roughly separated from the recycle stock (butanes, butenes, propane and



Courtesy "National Petroleum News"

FIGURE 14.—Flow Chart of the Unitary Process.

propene). In the rerun tower the synthetic material is separated into gasoline and heavy residuum of 18-20 A.P.I. gravity. The results of the operation are as follows:

Fresh feed (gallons butanes per day)	40,000
10-lb. Reid V.P. 400°E.P. gasoline	17,000
Residuum (18-20 A.P.I. gravity)	650
Residue gas (cu. ft.)	1,900,000

The residue gas is produced under 500 pounds per square inch gauge pressure. The octane number of the gasoline is 78 (Motor Method).

The utility requirements for the plant are:

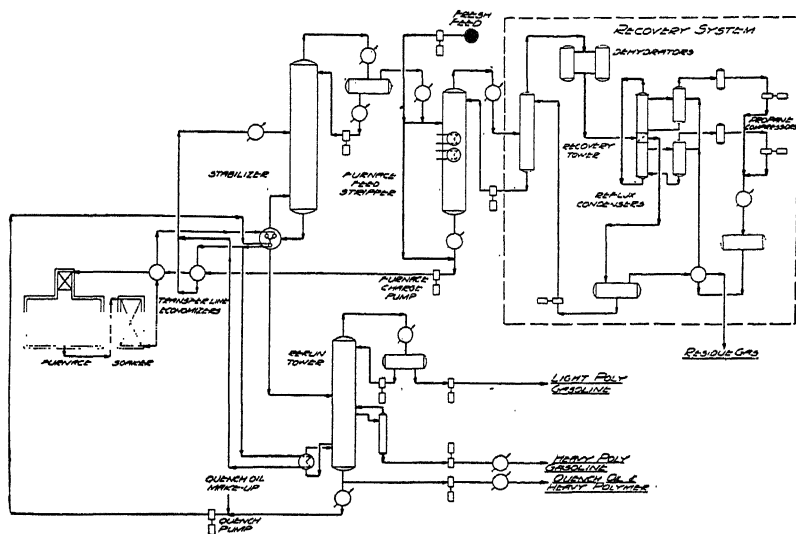
Steam (175 lbs. pressure)	4,500 lbs./hour
Water (maximal temp. 85°F.)	3,000 G.P.M.
Fuel gas	1,300,000 cu. ft./day
Electricity (lighting only)	15 KW

The fuel gas quantity given above includes all requirements with the exception of steam production.

The aforementioned data show that the consumption of fuel is very high in this process, amounting to 35 per cent by weight of the charge. Installation costs of a plant of this design will lie between \$600 and \$700

per barrel per day of 10-lb. R.V.P. gasoline, or about \$263,000 for a plant of the capacity given above.

More complete data are given for a large thermal conversion unit of the Humble Oil and Refining Company at Baytown, Texas. The flow sheet of the plant is given in Figure 15. In contradistinction to the small unit mentioned above, the Humble unit uses the recovery system



Courtesy "National Petroleum News"

FIGURE 15.—Flow Chart of the Unitary Process.

operating at low temperatures. The capacity of the unit is from 6000 to 9500 barrels per day of fresh feed. The fresh and recycle stock, from 28,000 to 35,000 barrels per day, preheated in heat exchangers by the furnace outlet streams, is pumped to the furnace. The flow through the heating part of the furnace is in four parallel coils, and in the soaking section in eight parallel coils. The outlet furnace stream is cooled in heat exchangers, in a reboiler, then by quenching oil and finally in a cooler before the inlet into the stabilizer. In the stabilizer a bottom product is separated from an overhead distillate which is free from hydrocarbons containing five or more carbons. The bottom product is introduced into the rerun tower where the heavy fractions above 400°F. are separated from the gasoline. The overhead distillate from the stabilizer is mixed with the fresh feed, if necessary, and enters the furnace stripper, where the furnace feed (C_4 and C_3 hydrocarbons) is separated from the lighter hydrocarbons. The lighter hydrocarbons, containing also C_4 and C_3 hydrocarbons, are treated in the low-temperature recovery system, where the C_4 and a part of the C_3 hydrocarbons are recovered by fractionation at low temperatures and returned to the furnace feed

stripper. The uncondensed vapors and gases from the recovery system form the residue gas. Typical operation conditions are given in Table 82. The yields for this unit at three different capacities are summarized in Table 83.

Table 82. Operating Conditions of Thermal Conversion of Gases.

Quantities		
Gross fresh feed (bbl./day)		6,000-9,500
Furnace charge (bbl./day)		28,000-35,000
10-lb. R.V.P. 400° E.P. poly. gasoline (bbl./day)		2,600-3,250
Gas, oil and tar (bbl./day)		140-250
Residue gas (cu. ft./day)		7,000,000-15,000,000
Temperatures and Pressures		
	Temp. (°F.)	Pressure (lbs./sq. in.)
Furnace inlet stream		
Furnace charge pump discharge	140	1950
Furnace inlet	600-620	
Furnace outlet stream		
Radiant section outlet	1000-1030	
Soaking section outlet	1010-1040	1700
Outlet transfer line exchangers	325-400	1000-1200
Primary tower		
Feed inlet	250-300	
Top	190-210	360-400
Reboilers	350-400	360-400
Gasoline tower		
Top	165	20
Bottom	350-450	20
Furnace feed stripper		
Top	135	340-380
Reboilers	200-210	340-380
Recovery tower		
Top	58-70	320-360
Bottoms	85-90	320-360
Reflux	7-30	320-360

Table 83. Yields of Gasoline from Butane Gas.

Gross fresh feed (saturated field butanes) (BSD)	6,000	8,000	9,500
Furnace charge rate (BSD)	34,000	34,000	34,000
Gross fresh feed (saturated field butanes) (BCD)	5,100	6,800	8,075
10-lb. R.V.P. 400°F., E.P. poly. gasoline (BCD)	2,200	2,572	2,735
Heavy polymer above 400°F. E.P.	115	182	212
Fuel gas produced MM B.t.u./CD	8,600	13,200	17,700

The yield of gasoline is from 43 to 34 per cent by volume with respect to the charging stock, and that of heavy residuum 2.7 per cent.

The no-profit value of butane is calculated from 1.545 to 1.615 cents per gallon, if the cost of gasoline produced is accepted as 6 cents per gallon.

The investment cost of the Multi-Coil and Unitary Process units is comparatively high due to the high temperatures and pressures used. According to Wade,⁵¹ the plant investment for a Unitary plant of a daily capacity of 2100 barrels is \$1,250,000.

High-temperature Aromatization of Gases

At very high temperatures of 800-1050°C. (1472-1922°F.) all paraffins, including methane and ethane, may be converted into aromatic hydrocarbons. The pressure in this process is low, from atmospheric to about 30-40 pounds per square inch gauge.

Dunstan and Howes⁷ give the following data on the conditions and yields of aromatic gasolines from paraffin hydrocarbons (Table 84). The time of the reaction is the same in all experiments.

Table 84. Yields of Aromatic Gasolines from Paraffin Hydrocarbons.

Hydro-carbon	Temp. (°C.)	Yields				Residue Above 200°C. (Gals./1000 cu. ft.)	
		Total (Gals./1000 cu. ft.)	Total (% by wt.)	—200°C. E.P. Benzol— (Gals./1000 cu. ft.)	(% by wt.)		
Methane	1050	0.44	8.8	0.3	4.7	0.14	4.1
Ethane	900	2.1	21.9	1.5	16.9	0.6	5.0
Propane	850	3.25	23.09	2.4	18.4	0.85	4.69
Butane	850	4.6	24.55	3.4	19.8	1.2	4.75
Ethene	800	3.15	36.1	2.4	28.8	0.75	7.3
Propene	800	5.32	40.6	4.0	31.2	1.32	9.4
Butene	800	6.85	39.6	5.1	30.7	1.75	8.9

The comparatively low yields of aromatics from paraffins, particularly from methane, should be mentioned.

The fractions 200°C. E.P. or benzols produced at 800°C. and higher are very aromatic. Their specific gravity at 60°F. is above 0.870, bromine number 30 or lower, octane number 87.7-104.1 (Motor Method). The benzene fraction boiling from 70-90°C. is predominant, amounting to 70-80 per cent of the total benzol. The residuum gases contain a large proportion of methane and hydrogen. For instance, the residual gases produced after the treatment of propane and butane at temperatures of 750-900°C. and pressures of 5-100 pounds per square inch gauge, contain:

Hydrogen	10-15	%	by volume
Methane	50-65	"	"
Ethane	0-10	"	"
Ethene	20-25	"	"

The process has very serious drawbacks from the engineering standpoint. The extremely high temperatures employed require the use of special expensive alloys. Even 18-8 chromium nickel steel gives satisfactory results only for temperatures not exceeding 650°C. (1202°F.), but reasonable tube life at temperatures up to 900°C. (1652°F.) can be obtained by the use of 25-20 chromium nickel steel, such as Hadfields H.R.3 or Krupp N.C.T.3.

The use of a recuperator furnace, incorporating fire-clay, silicon carbide or silicon blocks, was unsuccessful on the ground of fragility, low heat transfer, and leakage between the recuperator blocks.

The formation of aromatic hydrocarbons in pyrolysis of methane and other low molecular weight paraffins is a result of secondary reactions described in Chapter 1. Ethene, ethane and acetylene are formed in the first stages of pyrolysis of methane. At high temperatures, low pressures and short reaction times the formation of acetylene from methane may be a predominant reaction, causing a conversion of 50 per cent and more of the methane into acetylene.

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Chapter 3

Fundamental Factors of Hydrogenation

TEMPERATURE-PRESSURE CONDITIONS OF HYDROGENATION

Hydrogenation of petroleum products is a process closely connected with cracking. The temperature range of commercial hydrogenation, from 400 to 560°C. (752-1040°F.) overlaps the temperatures used in mixed-phase cracking. As a result, the extent to which cracking reactions take place under the conditions of hydrogenation depends mostly on the temperature of the process.

Low-temperature hydrogenation is not employed commercially, since this process does not yield gasoline, which is a principal product of cracking and hydrogenation. In addition to this, such catalysts as platinum or nickel, very active at low temperatures, are extremely sensitive to the poisonous effect of sulphur compounds present in petroleum oils, and rapidly lose their activity as a result of poisoning.

The high-temperature conditions of modern hydrogenation of petroleum oils necessitate the use of high hydrogen pressures. It should be remembered that the free energy, ΔF° , of hydrogenation of unsaturated and aromatic hydrocarbons is positive at temperatures above 500°C. (932°F.) for olefins and above 300°C. (572°F.) for aromatics. Only by the use of high pressures of hydrogen can the free energy of hydrogenation be made negative at high temperatures, according to equation (28). The pressures in commercial hydrogenation are usually as high as 200 atmospheres. The rate of hydrogenation of certain sorts of coal and asphalts may be comparatively slow under pressures of 200 to 300 atmospheres. For these materials such high pressures as 700 atmospheres at 500°C. (932°F.) are used in commercial operation, the process being performed on a large scale in reaction chambers of 10 cubic meters capacity.²²

A partial high-temperature hydrogenation can be performed under low pressures of hydrogen from 5 to 20 atmospheres in the presence of very active molybdenum and tungsten catalysts [Krauch and Pier, U.S.P. 2,132,855 (1938)]. The temperature of the process is from 400 to 480°C. (752 to 896°F.). As the data given above show, at least a partial hydrogenation of olefins and other aliphatic unsaturates is thermodynamically probable under these conditions, while even a partial hydrogenation of aromatics seems to be impossible. The products obtained contain an appreciable quantity of unsaturates, about 10 per cent or more.

The rate of hydrogenation under these conditions is low as compared with that of high-pressure hydrogenation.

The process of commercial hydrogenation may be carried out at lower or higher temperatures of the above given temperature range. The moderate-temperature process involves the use of temperatures around 400°C. (752°F.), and short reaction times. Under these conditions and high hydrogen pressure, hydrogenation reactions predominate, and cracking reactions occur to a comparatively small extent. This process of non-destructive hydrogenation may be employed to alter the properties of petroleum products.

Moderate- and high-temperature destructive hydrogenation are performed at temperatures of 400-560°C. (752-1040°F.). The cracking reactions take place in this process, to a large extent yielding gasoline. Production of the highest possible yields of gasoline is the goal of this process. Due to the predominance of cracking reactions, the process is specified as destructive hydrogenation.

Moderate- and high-temperature destructive hydrogenation produce very high yields of gasolines. The properties of hydrogenation gasolines depend on the temperature conditions as well as on the catalysts employed. The moderate-temperature process gives paraffinic gasolines, and the high-temperature process yields highly aromatic naphthas.

If the temperature range of cracking and hydrogenation is practically the same, the high pressure of hydrogen is a distinct feature of hydrogenation. Another important feature is the use of catalysts, which will be studied in the next section.

The turbulent flow of the heterogeneous mixture of hydrogen and charging stock may play an important part in hydrogenation. Morgan and Veryard¹⁷ conducted the hydrogenation of tars in a pipe system under the conditions of stream-line and turbulent flow. Other conditions being the same, the yields of gasoline depended upon the character of flow in the pipe system. The yield of gasoline from a low-temperature tar was more than doubled by changing the flow from non-turbulent (Reynolds number * 1000) to turbulent (Reynolds number 5600). In addition, the increase in the degree of turbulence, or in the Reynolds number, from 5500 to 11,000 doubled the yield of gasoline. The low-temperature tar was hydrogenated under conditions of turbulent flow without a catalyst. These experiments seem to be of great importance to the further development of commercial hydrogenation. At the present time the hydrogenation process in reaction chambers is performed under the conditions of stream-line flow.

* Reynolds number, R , is expressed by the following equation:

$R = \frac{vDd}{e}$, where v is the linear velocity of the charge, D the diameter of the pipe, d the density of the charge, and e the absolute viscosity.

Catalysts of Hydrogenation

The high pressure-temperature hydrogenation of petroleum products may be performed non-catalytically. The use of catalysts, however, enormously increases the rate of hydrogenation. Catalysts are employed in all commercial processes. The basic patents for these have been issued to Krauch and Pier [U.S.P. 1,890,434 and 1,890,436 (1932)].

The first basic stage of the commercial development of hydrogenation was made by Bergius. Ferric oxide was used in the Bergius process to remove part of the sulphur. Actually the ferric oxide and sulphides formed in the process acted as catalysts, but the catalytic activity of these compounds was very poor. The further development of catalysts for commercial hydrogenation of coal and petroleum products was due mostly to the extensive research of I. G. Farbenindustrie. Catalysts resistant to sulphur and stable in operation were discovered and introduced into commercial practice.

There is no general theory of heterogeneous catalysis, and the development of hydrogenation catalysts is rather a matter of guess and gambling, as in other fields of catalytic processes. The activity of a hydrogenation catalyst depends on its nature, the nature of the product to be hydrogenated, the temperature and the method of preparation.

Promoters may considerably increase the activity of a catalyst. The action of promoters was first discovered for the synthesis of ammonia from hydrogen and nitrogen. The catalytic action of iron is greatly increased when the catalyst contains a small amount of oxides of aluminum, silicon, thorium, zirconium or cerium.

Mixed catalysts may have a mutual promoting action, and as a result, the activity of a mixed catalyst may be greater than would be expected on the grounds of simple additive effects. The carriers or supporters are supposed to be non-active media for a catalyst, but a certain promoting action is frequently observed in the use of carriers. No definite border line can be drawn between carriers and promoters.

It should be kept in mind that the reactions catalyzed by a heterogeneous catalyst take place on the surface of the catalyst between the molecules adsorbed by the surface. Thus an indirect relationship between the activity of a hydrogenation catalyst and its capacity to adsorb hydrogen (or the heat of adsorption) could be expected. It is well known, for instance, that the most powerful catalysts of hydrogenation, powdered platinum and palladium, readily adsorb hydrogen.

The data of Griffith^{7a} on the adsorption of hydrogen by metallic oxides are given in Table 85.

The most active hydrogenation catalysts have the greatest values of adsorption of hydrogen. The change in adsorption with temperature is the most interesting and significant phenomenon. Such catalysts as cobalt have approximately constant values of hydrogen adsorption independently of the temperature. Such catalysts as alumina, vanadium

Table 85. Adsorption of Hydrogen on Oxides and Metals.

	20°C.	100°C.	cc. Adsorbed by 100 gr. of Catalyst			
			200°C.	300°C.	400°C.	450°C.
V oxide	33	27	30	490	1,950	1,974
Cr oxide	93	152	280	400	392	385
W oxide		3	76	57	38	210
Fe oxide	24	40	80	360	1,678	1,800
Co oxide	15	613	993	1,014	1,013	1,013
Th oxide	8	7	7	14	67	81
Ti oxide	24	20	17	131	151	156
Al oxide	13	16	20	21	922	1 865
Sn-Kaolin	78	68	67	92	268	547
Cd-Kaolin	28	33	47	100	185	190
Ce oxide	14	12	234	309	334	321
Mg oxide	19	17	21	22	65	65
Zr oxide	7	9		31	61	69

oxide, ferric oxide and tin adsorb hydrogen readily only at high temperatures which favor their catalytic action. As has been pointed out in Chapter 1, alumina and vanadium oxide are very active catalysts in high-temperature dehydrogenation. It is understood that the hydrogenation and dehydrogenation activity of a catalyst are equal, due to the reversibility of these reactions.

The action of promoters may also be closely connected with adsorption. Many hydrogenation catalysts activated with certain promoters adsorb hydrogen many times as fast as unpromoted catalysts, as can be seen from the data of Griffith and Hill,⁸ given in Table 86. On the other hand, the adsorption of catalysts is adversely affected by poisoning.

Table 86. Adsorption of Hydrogen on Promoted Molybdenum Oxide Catalyst; Silica as Promotor.

Catalyst, Si Atoms to 100 Mo Atoms	cc. Adsorbed per 100 parts	
	at 250°C.	at 450°C.
0	2.0	9.6
3.0	13.9	22.1
4.4	11.5	22.0
5.5	40.6	38.4
10.0		50.0

According to Taylor,²⁰ the absence of a direct relationship between the adsorption and catalytic activity is due to the dual nature of adsorption. The adsorption of gases at low temperatures does not change the "configuration" and activity of the adsorbed molecules. Only activated or chemical adsorption, taking place at comparatively high temperatures, is responsible for the activity of adsorbed gas and its catalytic action. The measurement of the adsorption at temperatures which are close to the working conditions gives a much closer relationship between adsorption and catalytic activity.

It is evident that the catalytic activity of a hydrogenation catalyst depends on the adsorption of hydrogen as well as of the hydrocarbons to be hydrogenated.

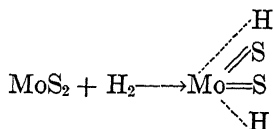
Various catalysts are recommended for the hydrogenation of oils, as well as coal and coal tars. The most important ones belong to the compounds of molybdenum, tungsten, chromium, vanadium, tin, zinc, iron,

cobalt and nickel. The aforementioned catalysts may be used alone or with other substances which play the part of promoters and carriers, such as clay, silica gel, alumina and magnesium oxide. When supported on magnesium oxide, kieselguhr, alumina, etc., catalysts frequently have greater activity than when used alone. Complex catalysts, such as molybdenum and zinc oxides, are also employed.

The compounds of tin are very effective catalysts for hydrogenation in semi-liquid phase. Stannous hydroxide, for instance, is many thousands of times more active than iron oxide in semi-liquid phase operation.

Compounds of molybdenum and tungsten, *i.e.*, oxides and sulphides, are the most effective catalysts in vapor- and mixed-phase hydrogenation. Molybdenum sulphide is more active than molybdic acid. Morgan and Veryard,¹⁶ for instance, found that the hydrogenation of a tar in the presence of molybdic acid took place only at 300°C. and 182 atmospheres pressure, while in the presence of molybdic acid and sulphur hydrogenation could be performed at 200°C. and 145 atmospheres pressure. Molybdenum sulphide is obtained *in situ* from molybdic acid by reaction of the charge with sulphur, if the content of sulphur is 0.5-1.0 per cent or more. In such cases the activity of the molybdenum catalyst increases in the first stage of the process following the transformation of molybdenic acid into molybdenum sulphide.

The active molybdenum sulphide catalyst is either MoOS or MoS₂.^{5a} Molybdenum disulphide is very stable at high temperatures even in the presence of high pressure hydrogen. On the contrary, molybdenum trisulphide is easily converted into molybdenum disulphide. Oxygen compounds of molybdenum are converted into MoOS and further into MoS₂ in the presence of sulphur or sulphur compounds. The mechanism of the catalytic action of molybdenum disulphide is the same as that of platinum or nickel catalysts. Hydrogen is chemically adsorbed by molybdenum disulphide, forming activated or free hydrogen atoms:



The sulphides of nickel and cobalt are fairly active hydrogenation catalysts in high temperature processes (above 400°C. or 752°F.). In contradistinction to this, they are almost inactive in hydrogenation at low temperatures and at low pressures of hydrogen.

It may be of interest to notice that not only the compounds of some heavy metals are active hydrogenation catalysts, but also some non-metals, particularly iodine, as well as some non-metallic compounds. I. G. Farbenindustrie (German P. 678,808, 1939) patented the use of halogen-containing catalysts, such as halogen compounds of sulphur, in hydrogenation. The halogens or metallic halides may be used also in

conjunction with metallic oxide or sulphide catalysts. Pier, Simon, and Eisenhut [U.S.P. 2,177,376 (1939)] recommend hydrogenating asphaltic materials in the presence of halogens, halogen compounds of sulphur, or phosphorus, and ammonium halides, and in the presence of volatile organic halogen compounds such as carbon tetrachloride. Other hydrogenation catalysts, as for instance metallic oxides or sulphides, can be employed simultaneously.

The data of Ormandy and Burns¹⁹ give an idea of the relative catalytic activity of various catalysts. A tar oil of specific gravity 0.970 was hydrogenated at 465°C. and 200 atmospheres pressure. The catalysts employed were on a support of a special alumino-ferrous material (Table 87).

Table 87. Destructive Hydrogenation in the Presence of Various Catalysts

Sulphur Added (% on Raw Material)	Hydrogen Consumed, lit./Kilo	Phenols in Product	—Yields (% by vol.)— TotalLight Gasoline	
Molybdenum Catalyst				
2	510	1.3	96.0	40.4
0	450	1.8	96.4	36.1
Tungsten Catalyst				
2	425	5.4	92.0	21.1
0	382	6.2	98.9	19.0
Cobalt Catalyst				
2	430		93.0	25.1
0	365		99.1	22.8
Nickel Catalyst				
2	440	6.9	97.8	26.5
0	420	8.9	96.3	20.7
Iron Catalyst				
2	370	9.3	95.1	16.2
0	350	9.6	83.5	15.5

The results indicate that molybdenum is the best catalyst for tar under the above conditions. Iron is the least active catalyst. The sulphur added has a positive effect on the catalysts used due to formation of more active sulphur compounds.

The use of carriers reduces considerably the charge of comparatively expensive catalytic materials. In addition to this, the catalysts on carriers can be easily regenerated. The maximum catalytic effect is frequently obtained with a catalytic mixture containing only a relatively small percentage of the catalyst on a carrier. The results of the hydrogenation of a low-temperature tar with various concentrations of molybdenum oxide catalyst on alumina gel carrier are given in Table 88.⁷ Thus the maximum catalytic effect of molybdenum catalyst on alumina is obtained with as low concentrations of the catalyst as 10-15 per cent with respect to the catalytic mass.

The catalysts may be used either in powdered form mixed with the oil, or in fixed state inside the reaction chambers. The first method is employed when hydrogenation takes place in the semi-liquid phase,

Table 88. Hydrogenation of Low-Temperature Tar with Molybdenum Oxide Catalysts on Alumina.

% Ammonium Molybdate	% Gasoline from Tar	% Gasol from Tar
5	27.0	53.4
10	33.1	58.2
15	34.1	63.1
20	35.7	65.2
25	33.9	62.7

particularly for coal. Fixed catalysts are used in both vapor phase and semi-liquid phase processes. The liquid products containing a considerable amount of asphaltic and resinous substances, such as tars, and heavy asphaltic and cracked residues, cannot be treated with fixed catalysts due to the deposition of carbonaceous substances on the catalyst. On the contrary, distilled high-boiling liquid products may be hydrogenated with fixed catalysts in the semi-liquid phase.

The advantages of fixed catalysts, as well as a broad use of this method in hydrogenation of petroleum products, are self-evident. In addition, the fixed catalysts produce a lesser yield of gases, particularly methane and ethane, and reduce the consumption of hydrogen.

The fixed catalysts may be used in the form of pellets consisting of the pure catalyst or they may be deposited on a granular porous carrier or supporter. Granular alumina gel ignited to a dull red, impregnated with ammonium molybdate and then heated to 500°C. in air, forms a very active supported molybdenum catalyst. In operation the catalyst is gradually transformed into still more active molybdenum sulphide, as has been mentioned above.

The pelleted and supported catalysts may have different activities, as the data of King and Cawley¹⁵ clearly show (Table 89).

Table 89. Comparison of Activities of Pelleted and Supported Molybdenum Catalyst.

	Pelleted		Supported	
	Yield of Gasoline (% by wt.)	Sp. Gr. (15°C.) of Liquid Products	Yield of Gasoline (% by wt.)	Sp. Gr. (15°C.) of Liquid Products
Hydrogenation of Low-Temperature Tar				
First Day	57.0	0.775	39.1	0.850
Second Day	40.9	0.826	38.1	0.862
Third Day	35.6	0.843	34.9	0.871
Fourth Day	33.8	0.860	34.3	0.875
Fifth Day	32.5	0.867	33.2	0.878
Hydrogenation of Middle Oil				
First Day	72.6	0.732	15.9	0.869
Second Day	73.2	0.736	19.8	0.860
Third Day	74.2	0.734	19.7	0.861
Fourth Day	75.6	0.735	41.0	0.833
Fifth Day	73.3	0.735	38.1	0.841

The temperature of the process was: 480°C. for the low-temperature tar, 400°C. for the middle oil with pelleted catalyst, 430°C. for the middle oil with supported catalyst in the first three days, 480°C. for the middle oil with supported catalyst in the last two days of the operation. The operating pressure was 200 atmospheres. The greater activity of the

pelleted molybdenum catalyst is clearly demonstrated by the figures of Table 89, particularly for the middle oil. The use of the pelleted catalysts, however, has a very serious drawback: they cannot be reactivated *in situ*. On the contrary, the reactivation of the supported catalysts by oxidation in air at 500°C. is an easy operation *in situ*.

When the catalysts are used in powdered form admixed with the charge, the concentration of catalysts with respect to the charge is low, usually not exceeding 1 per cent by weight. Such catalysts as tin compounds are admixed in lower concentrations, 0.5 per cent and less. Carriers may be successfully employed for powdered catalysts also.

In another method of operation, the powdered catalysts are not admixed with the feed, but are charged directly into the reaction chamber, where the concentration of the catalyst may be as high as 20-30 per cent with respect to the amount of oil in the chamber.

When fixed catalysts are employed, the total throughput of oil per volume of catalyst space per hour determines the activity of the catalyst. According to Haslam *et al.*,¹¹ the throughput of gas oils per volume of catalyst per hour is from 2 to 4 in commercial high pressure operation (Standard Oil Co. of N. J.). It is understood that these figures of the throughput ensure a high rate of hydrogenation and conversion in commercial operation. Under low hydrogen pressures the rate of hydrogenation is much slower. According to Krauch and Pier [U.S.P. 2,132,855 (1938)], the space velocity at pressures below 20 atmospheres is about $\frac{1}{8}$ per volume of catalyst per hour.

The life and deterioration of catalysts depend on the properties of the charging stock, temperature, reaction time and hydrogen pressure. The deterioration of catalysts is manifested in a progressive decrease in the yield of gasoline and in an increase in the specific gravity of gasoline, as well as of other products. Other conditions being equal, the deterioration is minimum for the stocks of low-boiling temperature range. Low temperature, small reaction time and high hydrogen pressure favor the long life of catalysts.

Sinnatt, King and MacFarlane²⁵ give the following data on the deterioration of a molybdenum catalyst during the first days of operation at various temperatures (Table 90). A tar of specific gravity 1.058, from

Table 90. Deterioration of Molybdenum Catalyst in Hydrogenation of Low-Temperature Tar.

Temp. (°C.)	Daily Increase in Sp. Gr. of Product	Daily Decrease in Gasoline Yield
400	0.0010	0.45
480	0.0028	0.7
510	0.0050	1.0

bituminous coal, was the charging stock in these experiments. The throughput was maintained at 10 volumes of charge per volume of catalyst per day. The operating pressure was 200 atmospheres.

When the pressure was raised to 400 atmospheres at 480°C., the daily

decrease in gasoline yield was reduced from 0.7 to 0.1 per cent a day and the daily increase in specific gravity was reduced from 0.0028 to 0.0010.

The figures of the deterioration of catalysts given above pertain to the hydrogenation of tars and heavy tar distillates. When hydrogenation is performed on the petroleum distillates, the life of catalysts may be reasonably long. Continuous operation periods of as long as a few months or even one year have been reported.

The reactivation of deteriorated supported catalysts by oxidation in air *in situ* completely restores the initial catalytic activity.

The method of preparation of the catalyst is of primary importance. The following data¹² illustrate the effect of this factor on the hydrogenation of a low-temperature tar at 480°C. and 200 atmospheres pressure:

Catalyst	A	B	C	D
Sp. Gr. of hydrogenated product	0.850	0.875	0.775	0.856
Yield (% by weight of fraction distilled below 200°C.)	39.1	33.8	57.0	37.1

The catalysts used were molybdenum sulphides prepared by the following methods. Catalyst A was alumina gel impregnated with 25 per cent of ammonium molybdate which was transformed into molybdenum sulphide in the process. Catalyst B was pelleted ammonium thiomolybdate. Catalyst C was pelleted molybdenum disulphide prepared by adding dilute sulphuric acid to a solution of molybdic acid in ammonium sulphide and heating the resulting precipitate in hydrogen at 427°C. Catalyst D was pelleted ammonium thiomolybdate preheated in hydrogen sulphide at 430°C. Catalyst C was not only the most active catalyst of those recorded, but also the most stable with respect to deterioration.

The catalysts and their modifications affect the yields as well as the properties and chemical composition of gasolines produced. Hall and Cawley⁹ give the following data on the chemical composition of hydrogenated gasolines produced from a middle oil of low-temperature tar with pelleted molybdenum sulphide catalyst, and the same catalyst supported on alumina gel (Table 91).

Table 91. Properties of Hydrogenated Gasolines from Low-Temperature Tar Produced in the Presence of Molybdenum Sulphide.

	Supported Catalyst	Pelleted Catalyst
Aromatics (% by wt.)	27	2
Naphthenes	66	50
Paraffins	7	48
Octane Number (C.F.R. Method)	70	70

The highly active pelleted catalyst produces a much greater amount of paraffins and a lesser amount of aromatics than the supported catalyst. The decrease in the percentage of aromatics in the presence of the pelleted catalyst is due to the hydrogenation of aromatics to naphthenes. The increase in the percentage of paraffins in the presence of pelleted catalyst is explained by the authors by the destructive hydrogenation of naph-

thenes to paraffins, with opening of the ring. It is of interest that the octane numbers of hydrogenated gasolines are not affected by the difference in the chemical composition.

Smith, Rall and Grandone^{25a} studied the activity of various catalysts in low-temperature and low-pressure hydrogenation of naphthalene. The temperature of the process was 95°C. Platinum, nickel and cobalt were the most active catalysts. Copper, iron, cadmium and molybdenum were not active at all under the conditions studied. The activity of a catalyst largely depends upon the supporter. Unsupported nickel, for instance, is much less active than nickel on granular charcoal or on acid-treated granular pumice. The formation of tetrahydronaphthalene is a predominant reaction in the presence of unsupported nickel, while decahydronaphthalene is readily formed in the presence of the supported catalyst.

Non-Destructive Hydrogenation

Non-destructive hydrogenation can be performed at temperatures not exceeding 350°C. or 662°F. The temperature of 350°C. may be considered as the upper limit of non-destructive hydrogenation, if the reaction time is reasonably short. The decomposition processes, however, take place at 350°C. to an extent depending on the reaction time and the catalyst.

In the presence of very active low-temperature catalysts, such as platinum, palladium or nickel, the hydrogenation of petroleum products can be performed at the comparatively low temperatures of 200°C. (392°F.) or less. The catalysts, however, are very easily poisoned by the sulphur compounds usually present in petroleum products.

Olefins are more easily hydrogenated than aromatic hydrocarbons. Waterman, Perquin and vanWesten³³ used a palladium catalyst and completely hydrogenated pentene at room temperature and atmospheric pressure. Under these conditions benzene was not hydrogenated at all. Vlугter³¹ hydrogenated cracked distillates at 300°C. and 100 atmospheres initial hydrogen pressure in the presence of molybdenum catalyst, and showed that only olefins were hydrogenated under these conditions, aromatics being unchanged.

Ipatieff and Corson¹³ hydrogenated a mixture of olefins and aromatics in the presence of nickel catalyst on kieselguhr at 20-50°C. and high hydrogen pressure (100 kg. per sq. inch initial), or at 115-175°C. and atmospheric pressure of hydrogen. In both operations only olefins were selectively hydrogenated.

Sachanen and Tarasov²³ investigated the low-temperature hydrogenation of a cracked kerosene at various temperatures and hydrogen pressures. The results are summarized in Table 92. The content of sulphur in the cracked kerosene was about 0.01 per cent. The process was carried out in the presence of 10 per cent of nickel-cobalt catalyst.

Table 92. Low-Temperature Hydrogenation of Cracked Kerosene.
I. Temp. 300°C. (572°F.). Initial Hydrogen Press. 200 Atm.

Time (hrs.)	Non-Catalytic ¹			Catalytic		
	Sp. Gr. at 20°C.	Aniline Point (°C.)	Iodine No.	Sp. Gr. at 20°C.	Aniline Point (°C.)	Iodine No.
0	0.818	61.5	35.5	0.818	61.5	35.5
0.5				0.817	65.6	12.7
1	0.817	61.9	31.7	0.810	65.2	11.1
2	0.817	61.9	25.9	0.813	64.5	9.8
3	0.817	62.3	19.4	0.811	65.7	7.8
∞	0.802	74.0	0.0	0.802	74.0 ✓	0.0

II. Catalytic Process at Various Temperatures and Pressures. Time, 3 Hours

Initial Hydrogen Pressure (atm.)	Maximum Pressure (atm.)	Temp. (°C.)	Sp. Gr. 20°C.	Aniline Point (°C.)	Iodine No.
0	0	300	0.818	61.5	35.5
50	97	—	0.815	64.1	18.0
100	180	—	0.815	69.5	12.6
150	272	—	0.815	65.1	9.3
200	368	—	0.811	65.7	7.8
150	279	200	0.817	63.2	16.9
150	249	250	0.816	65.1	11.4
150	262	275	0.816	64.9	10.9
150	272	300	0.815	65.1	9.3
150	273	325	0.814	65.5	5.8
			0.802	74.0	0.0

The total hydrogenation (time ∞) was performed in the presence of 2 per cent of powdered platinum at 300°C. under initial hydrogen pressure of 200 atmospheres for 2 hours. The totally hydrogenated product did not react with concentrated sulphuric acid.

The iodine numbers of hydrogenated products show that hydrogenation takes place at 200°C. and 200 atmospheres initial hydrogen pressure in both the catalytic and non-catalytic processes. The rate of hydrogenation in the catalytic process is three times greater than that in the non-catalytic.

The rate of hydrogenation increases with increasing temperature and hydrogen pressure, other conditions being equal. Partial hydrogenation in the presence of nickel-cobalt catalyst occurs at such low temperatures as 200°C.

Mostly olefins are hydrogenated in the presence of nickel-cobalt catalyst under the conditions of the low-temperature process. Aromatic hydrocarbons do not react with hydrogen to any extent under these conditions, as can be seen from the aniline points of hydrogenated products. The aniline points are only slightly above the initial aniline point and much lower than that of the completely hydrogenated product. Thus the process of low-temperature hydrogenation in the presence of nickel-cobalt catalyst is incomplete. Only with powdered platinum are olefins and aromatics completely hydrogenated.

These data show the difficulties encountered in the low-temperature hydrogenation of petroleum products containing even very small percentages of sulphur. The activity of such catalysts as cobalt or nickel,

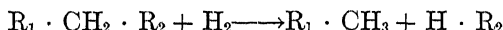
which are not resistant to sulphur, is impaired to a large extent by sulphur. As a result, the process is slow and not complete. The sulphur-resistant catalysts are not sufficiently active at the low temperatures of the process.

Thus in commercial practice, non-destructive hydrogenation is carried out at higher temperatures—about 400°C. (752°F.). Under these conditions, the rate of hydrogenation in the presence of sulphur-resistant catalysts is great, but the process is accompanied by cracking, producing low-boiling products. At a sufficiently short time of the process, the cracking reactions may be reduced to a minimum.

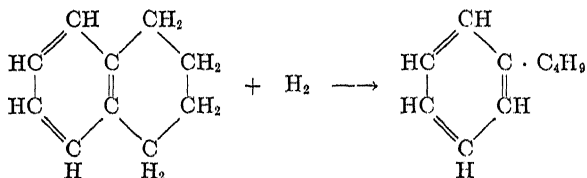
The low-temperature hydrogenation of iso-octenes into iso-octanes have been described in Chapter 1. It should be remembered that in this case the effective hydrogenation of olefins in the presence of nickel catalyst is obtained as a result of an almost complete desulphurization of the feed.

Cracking Reactions in Destructive Hydrogenation

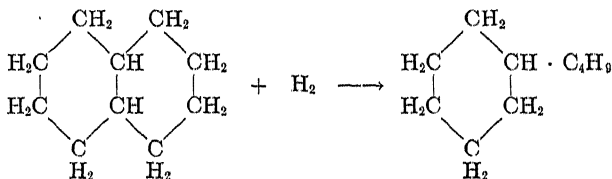
The mechanism of the decomposition reactions in destructive hydrogenation has been discussed in detail in Chapter 1. The paraffinic side chains of cyclic hydrocarbons, as well as the paraffins, are the most unstable constituents. They break down, forming paraffins and cyclic hydrocarbons with shorter side chains. Olefins are not formed in the hydrogenation, being hydrogenated to paraffins, as for instance,



In the second stage of hydrogenation naphthenes, as well as partially hydrogenated aromatics, break down in the hydrogenated ring, opening the ring and producing the derivatives of partially degraded hydrocarbons, for instance:



A similar reaction with naphthenes produces partially degraded naphthenes:



As a result, the initial stock is decomposed to paraffins, naphthenes

and aromatics of lower molecular weight and of less polycyclic structure. The derivatives of benzene formed are not hydrogenated to those of cyclohexane under high-temperature conditions of hydrogenation (above 500°C.). Thus highly aromatic gasolines can be produced from naphthenic or aromatic charging stocks.

Non-Catalytic Process

The temperature range of destructive hydrogenation, from 450-540°C. (842-1004°F.), favors the high rate of cracking reactions. In addition, some hydrogenation catalysts may also catalyze the cracking reactions.

Sachanen and Tilicheyev²⁴ investigated the kinetics of gasoline formation in the non-catalytic destructive hydrogenation of a paraffin distillate of specific gravity 0.872. The results obtained can be directly compared with those of simple cracking under the same conditions of temperature and time. The results of both processes are given in Table 93.

Table 93. Cracking and Destructive Hydrogenation of Paraffin Distillate.

Time (hrs.)	Cracking at 430°C. (806°F.) Gasoline Yield, 410°F. E.F. (% by vol.)	Destructive Hydrogenation at 430°C. (806°F.) Initial Hydrogen Pressure 100 Atm. Gasoline Yield, 410°F. E.F. (% by vol.)
0.5	18.8	9.4
1.0	33.0	
1.5	43.4	26.4
3.0		42.7
5.0	45.2	
6.0		50.8
9.0		49.1
12.0		51.0

Thus the course of formation of decomposition products during destructive hydrogenation is the same as during cracking. The yield of gasoline increases with time and reaches a maximum corresponding to 51 per cent by volume for the distillate investigated. When the process is continued, the yield of gasoline decreases due to the progressive decomposition of gasoline to gas.

A comparison of the results of cracking and destructive hydrogenation shows that during the first stages of the process the rate of decomposition in hydrogenation is smaller than in ordinary cracking. When the time of the process increases, the rates of formation of gasoline in hydrogenation and in cracking approach the same value. The same phenomenon was observed by Waterman and Perquin.³²

A slower rate of decomposition in hydrogenation may be explained by the higher thermal stability of paraffin hydrocarbons in comparison with unsaturated ones. The unsaturated hydrocarbons formed by decomposition are transformed into saturated ones by the reaction with hydrogen and are then decomposed more slowly in the further stages of process. The rates of formation of gasoline approach the same value in hydrogenation and in cracking, when the processes are prolonged, because in the

advanced stages of hydrogenation more material is available for conversion into gasoline than in the case of cracking, due to suppression of condensation reactions and coke formation.

Thus in non-catalytic destructive hydrogenation very high yields of gasoline cannot be produced in a once-through operation. The maximum yield of gasoline given above, about 51 per cent, is accompanied by considerable gas formation, up to 25 per cent of the charging stock. The yields of gasoline per pass without excessive gas formation should be from 40 to 45 per cent by volume. As in cracking, the final high yields of gasoline can be produced in the recycle operation. It should be remembered that the allowable yields of gasoline per pass in cracking of gas oils do not exceed 20-25 per cent on account of coke formation, appreciable with the higher yields. In non-catalytic destructive hydrogenation the allowable yields per pass are much greater due to the suppression of coke formation. An excessive gas formation, due to partial decomposition of gasolines to gases, is another drawback to this process, limiting the allowable yields per pass to 40-45 per cent by volume.

Further experiments at various temperatures clear up the influence of temperature on gasoline formation in the non-catalytic process with the same paraffin distillate.

The purpose of these experiments was to investigate the kinetics of the decomposition reactions in hydrogenation under simplified conditions, *i.e.*, in the absence of catalysts.

The results of three series of experiments for the temperature range 380-480°C. (716-896°F.) and various times are given in Table 94. The

Table 94. Comparative Rates of Decomposition at Different Temperatures in Non-Catalytic Destructive Hydrogenation; Initial Hydrogen Pressure 100 Atm.

Series	Temp. (°C.)	Time (hrs.)	Yield of Gasoline, 410°F. E.P. (% by vol.)
I	380	18	7.8
	405	3	7.8
	430	0.5	9.4
II	405	18	50.8
	430	3	42.7
	455	0.5	42.2
III	430	6	50.8
	455	1	48.7
	480	11 min.	47.0

yields of gasoline are approximately equal in each series of experiments. The data show that raising the temperature of the process 25°C. decreases its duration sixfold for the same yield of gasoline. Thus the temperature coefficient of gasoline formation in destructive hydrogenation is approximately the same as in cracking (about 1.9 for the lower temperatures).

Catalytic Process

The rate of decomposition reactions in catalytic hydrogenation usually increases as compared with the non-catalytic process, due to the simul-

taneous catalytic action of hydrogenation catalysts upon the cracking process. It should be noticed, however, that the high rate of gasoline formation in catalytic hydrogenation, particularly for heavy products, is due partially to the decomposition of hydrogenated cyclic hydrocarbons, which are formed by hydrogenation and yield an additional amount of gasoline according to equations 29-31.

According to Szayna,²⁸ the rate of gasoline formation from paraffin wax and oils in catalytic hydrogenation is only slightly above that obtained in the non-catalytic process, with the exception of a heavy cracked oil, which gives a considerably higher rate in catalytic hydrogenation. Candea and Sauciu⁴ obtained similar data on the catalytic and non-catalytic hydrogenation of a paraffin wax. On the contrary, Tropsch³⁰ and King¹⁴ have found that the rate of gasoline formation from a gas oil and low-temperature tar in catalytic hydrogenation is much higher than in the case of the non-catalytic process. These data are summarized in Table 95. The following conclusions may be drawn from them:

Table 95. Comparative Data on the Rate of Gasoline Formation in Non-Catalytic and Catalytic Hydrogenation.

Temp. (°C.)	Time (hrs.)	Yields of Gasoline (% by wt.)			Ref.
		Non-Catalytic	Catalytic	Catalyst Used	
		Cracked Oil, Sp. Gr. 0.954			
480	2¼	23.8	44.3	NiO-MoO ₃	Szayna ²⁸
		Straight-run Residuum, Sp. Gr. 0.935			
480	1	36.8	37.5	NiO-MoO ₃	Szayna ²⁸
		Paraffin Wax			
420	1	14	17	MoS ₃	Candea <i>et al.</i> ⁴
430	1	21	25	MoS ₃	
440	1	31	38	MoS ₃	
		Gas Oil			
440	1	21.1	55.3	(NH ₄) ₂ MoS ₄	Tropsch ³⁰
		Low-Temperature Tar, Sp. Gr. 1.060			
450		6	27	MoS ₃	King ¹⁴

1. The rate of cracking in catalytic hydrogenation is somewhat greater than in non-catalytic. Thus hydrogenation catalysts also catalyze cracking reactions.

2. The effect of catalysts on the rate of cracking in hydrogenation is comparatively small for paraffin wax and light gas oils.

3. The effect of catalysts on the rate of cracking in hydrogenation is great for heavy products containing a large proportion of aromatic hydrocarbons.

Certain hydrogenation catalysts have a very marked splitting action. In their presence destructive hydrogenation can be performed at such low temperatures as 343-427°C. (650-800°F.).²⁷

The temperature has a very strong influence on the rate of gasoline formation in the catalytic process. The following data of King and Cawley¹⁵ illustrate the connection between gasoline formation and temperature (Table 96).

Table 96. Gasoline Formation in Catalytic Hydrogenation of Low-Temperature Tar. Hydrogen Pressure 200 Atmospheres. Molybdenum Catalyst.

Temp. (°C.)	Sp. Gr. of Hydrogenated Tar (15°C.)	Yield of Gasoline to 200°C. (% by wt.)
...	1.049	7.1
300	1.040	7.2
350	0.997	13.4
390	0.942	19.7
430	0.900	30.4
450	0.888	34.2
480	0.867	40.5
510	0.847	46.0

Neither gasoline formation nor hydrogenation take place to any extent at 300°C. Both processes start at 350°C., and their rate gradually increases with increasing temperature.

Another factor affecting the rate of cracking in catalytic hydrogenation is hydrogen pressure. The data of King and Cawley demonstrate clearly the effect of hydrogen pressure (Table 97). A molybdenic

Table 97. Effect of Hydrogen Pressure on Gasoline Formation in Catalytic Hydrogenation of Low-Temperature Tar.

Hydrogen Press. atm.)	Sp. Gr. of Hydrogenated Product at 15°C.	Yield of Gasoline to 200°C. (% by wt.)
Temperature 483°C.		
100	0.895	35.4
150	0.886	36.3
200	0.867	40.5
400	0.847	42.2
Temperature 510°C.		
200	0.858	46.5
400	0.816	56.0

catalyst was used in these experiments, and the reaction time was the same for all. The total pressures are assumed to be equal to the hydrogen pressures due to the excess of hydrogen used in the process.

The effect of the hydrogen pressure is much greater at 510°C. than at 483°C. It should be kept in mind that at higher temperatures the free energy of hydrogenation, ΔF° , is strongly positive (eq. 27), and that ΔF° may be negative only under very high pressure of hydrogen (eq. 28). As a result, yields of gasoline in hydrogenation at high temperatures, particularly from aromatic products, can be obtained only under high pressures of hydrogen.

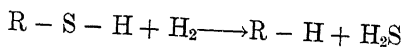
In general in catalytic destructive hydrogenation the rate of decomposition is appreciably higher than in the case of the non-catalytic process, depending upon the catalyst. The formation of gasoline in catalytic hydrogenation is greater, even in the initial stages of the process, than is the case with cracking. As a result, the allowable yields per pass in catalytic hydrogenation may be considerably higher. Under moderate temperature-time conditions and in the presence of active catalysts, such a high yield per pass as 60-65 per cent can be easily obtained without

excessive gas formation. Therefore, the extent of recycling in catalytic hydrogenation is much smaller than in cracking.

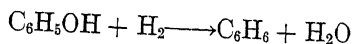
Decomposition of Oxygen and Sulphur Compounds

The decomposition of oxygen and sulphur compounds present in oils in the destructive hydrogenation process is a very important reaction, resulting in partial or almost complete deoxygenation and desulphurization of hydrogenated products. As a general rule, the oxygen and sulphur compounds of oils react with hydrogen very easily, forming hydrocarbons and water or hydrogen sulphide. These reactions take place much more easily than the hydrogenation of aromatic hydrocarbons and even of olefins.

Such sulphur compounds as mercaptans and sulphides react with hydrogen according to the equation:



The same reaction proceeds with phenols:



The last reaction is of importance to low-temperature tars containing a considerable proportion of phenols, but not important to petroleum products. Cresylic acid, for instance, is catalytically hydrogenated to hydrocarbons under a pressure of 150 atmospheres and at temperatures of from 380 to 400°C. [Krauch and Pier, U.S.P. 1,890,434 (1932)].

As the data of Pier²¹ show, the desulphurizing effect of hydrogenation takes place under comparatively moderate hydrogen pressures (Table 98).

Table 98. Hydrogenation of Cracked Gasoline.

Hydrogenation Pressure	Original Gasoline	—Hydrogenated Gasoline— 50 atm.	200 atm.
Specific Gravity (20°C.)	0.743	0.742	0.738
Iodine Number	106	20	15
Sulphur (%)	1.00	0.04	0.007
Color	Yellow	Alm. W.W.	W.W.
Odor	Sour	None	None

Thus, under a hydrogenation pressure of 50 atmospheres, the decomposition of sulphur compounds is almost complete, while the hydrogenation of unsaturated hydrocarbons proceeds only to 80 per cent.

The high molecular weight polycyclic oxygen and sulphur compounds, such as resins and asphaltenes, are hydrogenated in the first stages of the process and undergo gradual decyclization according to the general scheme, *e.g.*, eq. 29-31. Thus, desulphurization occurs simultaneously with the decyclization. As a result, the resinous and asphaltic materials are transformed into hydrocarbon oils of lower molecular weight.

Krauch and Pier [U.S.P. 1,890,436 (1932)] described the hydrogenation of a Mexican asphalt dissolved in cyclohexane (equal parts by weight) under a pressure of 200 atmospheres and a temperature of about

450°C. over molybdenum catalyst. The cyclohexane was recovered unaltered, while the asphalt was completely converted into a thin oil, free from oxygen compounds. Pier, Simon and Eisenhut [U.S.P. 2,177,376 (1939)] hydrogenated a mixture of resins and asphalts, precipitated from a crude by liquid propane, at 425°C. during 90 minutes under high pressure in the presence of 1.15 per cent of ammonium chloride. The cracking was very moderate under the above conditions. About 15 per cent of the synthetic products obtained distilled up to 300°C. The rest was a heavy oil of specific gravity 0.940 at 100°C., containing only 4 per cent of asphalt. Halogen compounds seem to be very effective catalysts in non-destructive hydrogenation of asphalts. The content of sulphur and coke-forming constituents decreases markedly after hydrogenation.

As will be seen later, a more or less selective hydrogenation and elimination of sulphur and asphaltic compounds under moderate temperature conditions may be obtained in commercial hydrogenation processes.

Aromatization and Condensation Reactions in Destructive Hydrogenation

The aromatization and condensation processes in hydrogenation are affected by hydrogen to a much greater extent than the decomposition reactions which have been discussed in the previous sections.

The presence of hydrogen in cracking affects the extent of cyclization due to the conversion of olefins into paraffins which are not cyclized in the presence of hydrogen. Waterman and his associates³⁴ have shown that the ring formation in cracking of a paraffin wax or hexadecane can be controlled and even prevented in the presence of high pressure hydrogen and active catalysts, and that a considerable cyclization takes place in plain cracking under the same conditions of temperature and time.

As has been stated in Chapter 2, the degree of condensation reaction is indicated by the specific gravities of residues remaining after distillation of the gasoline and the recycle fractions formed (to 300°C. or to 572°F.), since high molecular weight aromatic condensation products are concentrated chiefly in residues. In addition, formation of coke is an indication of advanced condensation processes. The data of Sachanen and Tilicheyev,²⁴ given in Table 99, show the influence of hydrogen pressure on the condensation processes taking place in non-catalytic destructive hydrogenation of a paraffin distillate of specific gravity 0.873 at 425°C. (797°F.). These data clearly indicate the gradual decrease in specific gravity of residues and of coke formation with increasing hydrogen pressure, other conditions being the same. Coke formation under the most severe conditions employed (6 hours at 430°C.) is almost completely suppressed under an initial hydrogen pressure of 100 atmospheres or an operating pressure of 250 atmospheres. The aromatization and condensation reactions, however, are only suppressed and not completely eliminated. The specific gravity of residues increases with in-

Table 99. Aromatization and Condensation Processes in Non-catalytic Destructive Hydrogenation of Paraffin Distillate.

Initial Hydrogen Press. (atm.)	Yield of Gasoline (% by vol.)	Sp. Gr. of Hydrogenated Residuum at 15°C.	Yield of Coke (% by wt.)
Temperature 430°C. (806°F.), Reaction Time 1 Hour			
0	33.2	0.956	0.73
25	30.8	0.913	0.02
50	32.4	0.900	0.00
200	16.7	0.909	0.00
Temperature 430°C. (806°F.), Reaction Time 1.5 Hours			
0	43.6	1.005	2.9
70	29.9	0.907	0.18
100	26.4	0.891	0.01
Temperature 430°C. (806°F.), Reaction Time 3 Hours			
0	44.2	More than 1.0	5.00
25	46.9	1.025	4.00
50	48.2	0.991	3.00
100	42.7	0.940	0.10
150	43.2	0.918	0.00
200	42.3	0.900	0.00
Temperature 430°C. (806°F.), Reaction Time 6 Hours			
00	46.3	More than 1.0	9.00
100	50.8	0.966	0.02
150	52.8	0.960	0.05

creasing severity of the treatment. Under the most severe conditions, the specific gravity of the residues is as high as 0.960, indicating appreciable condensation and aromatization reactions.

The character of the condensation and aromatization reactions in destructive hydrogenation has been determined as a result of fractionation of the hydrogenation residues after very advanced hydrogenation of the paraffin distillate. The data given in Table 100 are compared with the distillation of the virgin paraffin distillate. They show that the fractions

Table 100. Distillation of Paraffin Distillate and Its Hydrogenation Residue Pressure.

Boiling Range (°C.)	Paraffin Distillate Virgin		Residue after Hydrogenation at			
	%	Sp. Gr.	25 Atms.		150 Atms.	
			%	Sp. Gr.	%	Sp. Gr.
Below 200	7.0	0.850	43.1	0.970	28.6	1.00
200-250	42.5	0.863	15.5	1.050	42.9	1.06
250-300	34.7	0.892	17.2	1.090	13.8	1.11
300-350	4.6	0.907	8.6	1.120	11.2	
Above 350	10.7	0.927	13.8		2.0	

from the hydrogenation residues are of considerably lower molecular weight and boiling range than those from the starting material. Thus, the reactions of the formation of high-boiling and high molecular weight products are almost absent under the conditions of hydrogenation. The increase in specific gravity of the hydrogenation residues and their fractions is due to aromatization of the hydrocarbons.

These conclusions are in full accord with the mechanism of the reactions which occur in cracking and hydrogenation. Polycyclic aromatic hydrocarbons of high molecular weight are condensed in cracking to heavy

and high-boiling products of condensation, and finally form coke. The same hydrocarbons are partially hydrogenated in destructive hydrogenation, forming polycyclic hydrocarbons with partially hydrogenated rings. These hydrocarbons are thermally unstable, and are decomposed in the presence of hydrogen, opening the hydrogenated ring and forming the derivatives of less cyclic aromatic hydrocarbons. As a result of these reactions, the boiling range of polycyclic fractions is considerably lowered, as has been found experimentally.

The catalysts in destructive hydrogenation only accelerate the hydrogenation reactions, not affecting the general character of the process. In the presence of catalysts the specific gravities of hydrogenation residues are lower due to a larger extent of hydrogenation. Some data of Szayna²⁸ on the action of catalysts upon hydrogenation are summarized in Table 101.

Table 101. Non-catalytic and Catalytic Destructive Hydrogenation of Petroleum Products.

	Non-catalytic	Catalytic
Straight-run Residuum, Sp. Gr. 0.935		
Catalyst (% by wt.)	None	MoS ₃ + Ni, 4%
Temperature (°C.)	480	480
Time (minutes)	63	65
Sp. Gr. of Synthetic Crude	0.833	0.825
Yield of Gasoline (% by wt.)	36.8	37.5
Sp. Gr. of Residue	0.980	0.956
Cross Residuum, Sp. Gr. 0.954		
Catalyst (% by wt.)	None	MoS ₃ + Ni, 8%
Temperature (°C.)	480	482
Time (minutes)	135	135
Sp. Gr. of Synthetic Crude	0.893	0.806
Yield of Gasoline (% by wt.)	23.8	44.3
Sp. Gr. of Residue	0.985	0.954

The figures of Table 101 show clearly that in catalytic hydrogenation the specific gravity of residues is invariably considerably lower than in the non-catalytic process corresponding to a greater extent of hydrogenation.

The extent of aromatization depends upon the temperature, the hydrogen pressure, and the activity of catalysts. At moderate temperatures, below 450°C., and at high pressures, in the presence of very active catalysts, the extent of aromatization may be small, and the hydrogenation reactions may be predominant. At high temperatures, above 500°C., and in the presence of moderately active catalysts, the reactions of dehydrogenation and aromatization take place readily, forming highly aromatic gasolines.

The destructive hydrogenation of such distilled products as gas oils and paraffinic distillates can be performed without catalysts. This depends upon the chemical composition of such distillates, containing relatively small amounts of highly polycyclic aromatics and asphaltic materials which condense rapidly to form coke. Nevertheless, the catalysts are

always used in commercial destructive hydrogenation of distillate oils. In the presence of catalysts the yields of gasoline are higher and the gas formation is lower, due to the use of less severe temperature-time conditions. On the other hand, much lower pressures can be employed in the catalytic process.

If the petroleum product is heavy and residual, and contains a considerable quantity of highly polycyclic aromatic hydrocarbons, resins and asphalts, then condensation reactions and coke formation may take place in the early stages of the process. For such products the use of catalysts becomes unavoidable in order to speed up the hydrogenation of polycyclic hydrocarbons and asphaltic materials before any appreciable condensation and formation of coke take place. Such products as heavy still bottoms, cracking residues, tars, etc., can be hydrogenated successfully only in catalytic operation.

Thermal Effect of Hydrogenation

In contradistinction to cracking, the thermal effect of hydrogenation is strongly positive. Even in destructive hydrogenation the negative thermal effect of cracking reactions is more than counterbalanced by the positive effect of the hydrogenation reactions in process, and the total thermal effect becomes positive. Thus, an increase in temperature takes place as the process of hydrogenation is performed in the reaction chamber. For this reason, the temperature of the charge entering the reaction chamber should be comparatively moderate in order to keep the reaction temperature within the desired range. As will be seen later, the reaction chambers are provided with a means of cooling, involving the introduction of hydrogen into the chamber.

The thermal effect of hydrogenation of butenes and hexenes is, respectively, 570 and 350 Cal. per kilogram, and that of benzene and naphthalene (complete hydrogenation) is, respectively, 660 and 550 Cal. The high molecular weight derivatives of benzene and naphthalene, and the high molecular weight olefins, have of course lower values. It should be kept in mind that hydrogenation of aromatic hydrocarbons in commercial processes is only partial and, in addition to this, is accompanied by decomposition reactions absorbing heat. According to computations on the basis of the actual results of hydrogenation, the thermal effect of destructive hydrogenation is close to 300 Cal. per kilogram for highly aromatic or naphthenic petroleum products.

Recycling in Destructive Hydrogenation

As has been stated above, the yields per pass in catalytic destructive hydrogenation must not exceed 50 to 65 per cent in order to avoid excessive gas formation. A higher conversion is accompanied by excessive decomposition of the gasoline formed to gaseous hydrocarbons. Coke formation does not play any important part in destructive hydrogenation,

as it does in cracking. The final high yields of hydrogenated gasoline are obtained in the recycle operation.

In contradistinction to cracking, the permissible yields of gasoline per pass in destructive hydrogenation do not depend on the individual properties of the charging stocks. The high yields in a once-through operation up to 60 per cent by volume may be obtained from light gas oils, as well as from heavy tars of specific gravity 1.0 and higher. This remarkable difference between cracking and destructive hydrogenation is due, evidently, to the elimination of coke formation. The activity of catalysts is the principal factor determining the yields per pass. In the presence of very active catalysts, performing hydrogenation under moderate temperature-time conditions, the yields per pass may be as high as 65-70 per cent by volume.

Three consecutive stages of non-catalytic hydrogenation were studied for a paraffin distillate of specific gravity 0.873 in bomb operation.²⁴ The synthetic crude after the first hydrogenation was distilled off, and the total residuum above 200°C. was hydrogenated in the second stage. The residuum above 200°C. after the second operation was repeatedly hydrogenated. The results are summarized in Table 102.

Table 102. Repeated Hydrogenation of Paraffin Distillate.
Temperature 425°C. (797°F), Initial Hydrogen Pressure 150 Atm. Operating
Pressure 350 Atm.

No. of Operation	Time of Hydro- genation (hrs.)	Yields on Hydrogenated Products (% by vol.)				Yields on Charging Stock (% by vol.)			
		Gas + Loss	Gasoline	Sp. Gr. @ 150°C	Residue above 200°C	Sp. Gr. @ 150°C	Gas + Loss	Gasoline 410°F. E.P.	Residue
1	3	0.4	38.5	0.722	61.1	0.855	0.4	38.5	
2	6	10.6	49.0	0.730	40.4	0.918	6.4	30.2	
3	6	8.2	41.8	0.738	50.0	0.965	3.3	8.2	
Final Yields							10.1	76.9	13.0

These data give an idea of the magnitude of the yields of gasoline in hydrogenation, as a result of recycling. Even in the above non-catalytic operation, when the gas formation is large, the yield of gasoline after three consecutive hydrogenations is 77 per cent, plus 13 per cent of residue. The total conversion of the residue would increase the final yield to approximately 85-90 per cent.

In commercial catalytic recycle operation at moderate temperatures the final yields of gasoline are as high as 110-120 per cent by volume. At high temperatures (500°C. and higher) the final yields are appreciably lower, due to greater gas formation, and amount to 90 per cent.

The properties of gasolines and residues in consecutive repeated hydrogenation operations have the same trend as in the case of repeated crackings (Table 102). The specific gravity of hydrogenated gasolines and residues increases for each consecutive hydrogenation, corresponding to the increase in aromaticity of the products. The processes of aromatization take place in destructive hydrogenation as well as in cracking.

There is, however, a very substantial difference between the aromatization reactions in these two processes. As has been stated in the previous section, the hydrogenation residues do not contain high molecular products of aromatic condensation, as in the case of cracked residues. The high specific gravity of hydrogenated residues is due entirely to the aromatic hydrocarbons, of moderate molecular weight not exceeding that of the virgin stock.

Due to the high yields of gasoline in a once-through operation, recycling in destructive hydrogenation is used to a much less extent than in cracking. The recycle ratio (volume of recycle oil: volume of fresh feed) depends on the temperature-time factor of the process. In high-temperature destructive hydrogenation the recycle ratio is close to 1, while in the moderate temperature process it is 0.5 or even lower.

Selective Destructive Hydrogenation

The process of destructive hydrogenation may be carried out in a one-stage operation with recycling. This method of operation, however, has the same disadvantages as in the case of cracking. The destructive hydrogenation of the virgin oil, as well as of the recycle stock, is performed under the same conditions of temperature, pressure and time and in the presence of the same catalyst. In addition to this, the virgin oil may consist of various fractions differing in cracking and hydrogenation properties.

Selective hydrogenation is carried out under specific or selective conditions for distillates of different boiling range and properties. For example, a virgin heavy oil is hydrogenated in the first stage under comparatively mild conditions of temperature, not higher 440° (824°F.). The process takes place in semi-liquid phase. The catalyst used in this stage may be fixed, or powdered and mixed with the feed, depending on the coke-forming properties of the feed. After the first stage, the synthetic crude is separated by distillation into gasoline, an intermediate fraction boiling, for instance, up to 350°C. (662°F.), and residue. The residue may be combined with fresh feed as recycle stock. The intermediate fraction is hydrogenated in vapor phase at high-temperatures, up to 510°C. (950°F.) or higher, in the presence of another fixed catalyst.

On the other hand, the separation of the oil to be hydrogenated into various fractions can be performed in a preliminary distillation. In the simplest case the oil is separated into a gas oil of proper boiling range and a residuum. The gas oil is hydrogenated in vapor-phase at high temperature, and the residuum in semi-liquid phase under more moderate conditions.

As will be described later, the Standard Oil Company of New Jersey uses the narrow fractions from selective crudes, boiling up to about 450-550°F., for the production of hydrogenated aviation fuels. With this method, catalysts are very long lived; they may be used for a year without appreciable deterioration.

Consumption of Hydrogen

An excess of hydrogen is used in hydrogenation. The yields of gasoline, as well as other results of hydrogenation, depend largely not only upon the pressure but also upon the relative amount of hydrogen. If the molar ratio of hydrogen to charging stock is about 30, corresponding to 25 per cent by weight of hydrogen with respect to the charge, then a further increase in the ratio does not appreciably affect the gasoline yield and the properties of hydrogenation products. In practise, the relative amount of hydrogen used in the process is up to 1000 cubic meters per ton of charging stock, or up to 10 per cent by weight with respect to the charge.

Due to the excess of hydrogen used in the process, the hydrogenation gases contain a large percentage of unused hydrogen. For this reason, they are separated from the liquid synthetic crude and recycled to the reaction chamber, after the removal of the hydrogen sulphide formed. If necessary, the gases can be treated with solvents or oils to remove the more soluble hydrocarbon gases commingled with the hydrogen.

The consumption of hydrogen in hydrogenating petroleum products depends on the hydrogen content of the charging stock and on the yields of gasoline. The ultimate analysis of low specific gravity gasolines gives 15.6 per cent of hydrogen and 84.4 per cent of carbon, and that of charging stocks of specific gravity 0.92-0.94 gives 11.6 per cent of hydrogen and 88.4 per cent of carbon. A theoretically total conversion of this charging stock into hydrogenated gasoline would require 5 per cent by weight of hydrogen, or about 0.5 per cent per each 10 per cent of gasoline formed. The actual consumption of hydrogen is somewhat larger, due to the formation of gaseous hydrocarbons rich in hydrogen. The average consumption of hydrogen in the destructive hydrogenation of light gas oils is fairly close to the above figure, 0.5 per cent by weight per 10 per cent of gasoline. Heavier stocks consume more hydrogen. Ando¹ investigated the destructive hydrogenation of a low-temperature tar of specific gravity 0.966, containing 29.4 per cent of phenols. The calculation of the consumption of hydrogen, made by the author on the basis of Ando's data, gives the figure of about 1.1 per cent hydrogen per 10 per cent gasoline formed.

A description of the commercial methods of the production of hydrogen is beyond the scope of this book. It should be mentioned, however, that the most important sources of commercial hydrogen are: coke-oven gas, water gas and natural gas. Natural gas is reacted with steam in the presence of nickel or cobalt catalysts at temperatures of 800-1000°C. (1482-1832°F.), producing carbon monoxide and hydrogen. In the second stage the mixture of carbon monoxide and hydrogen is treated at temperatures of 400-600°C. (752-1112°F.), over iron oxide as catalyst. Under these conditions, carbon monoxide is oxidized to carbon dioxide at the expense of the oxygen of water, producing more hydrogen. Carbon dioxide is separated from hydrogen by chemicals or water.

The same process is applied to coke-oven or water gas for the oxidation of the carbon monoxide present in these gases to carbon dioxide, which can easily be removed.

The hydrogenation recycle gases usually contain a considerable amount of methane and ethane that can be used for producing the hydrogen required for hydrogenation. The amount of hydrocarbons in hydrogenation gases, however, produces only a part of the hydrogen consumed in the process.

The use of hydrogen increases the requirements of the steel employed in hydrogenation units. Plain-carbon steels cannot be used in the parts of hydrogenation units subjected to high temperatures and pressures. Under these conditions, hydrogen combines with the carbon of steel to form methane. As a result, the decarbonized steel is rapidly disintegrated, forming cracks and fissures. The main factor is the temperature. If the hydrogen pressure is high, decarbonization starts at temperatures of about 350°C. (622°F.) and rapidly progresses with increasing temperature.

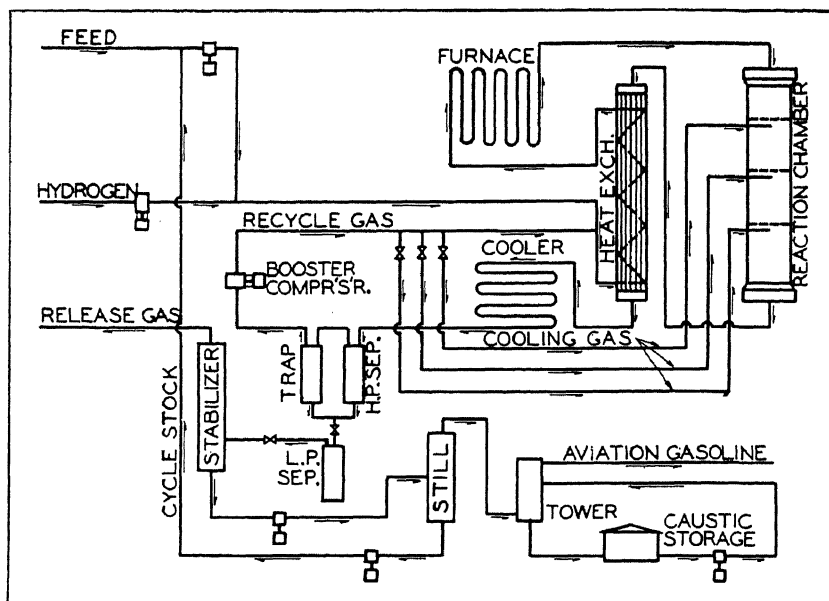
Chromium steels are resistant to hydrogen attack, the resistance being improved by increasing the proportion of chromium in the steel. A 3-per cent chromium steel may be used up to 400-450°C. (752-842°F.), and 6-per cent chromium steel up to 550°C. (1022°F.) under the pressures employed in commercial hydrogenation. The addition of tungsten, molybdenum and vanadium brings a further improvement in the resistance of steels to hydrogen. Low-carbon steels containing 6 per cent of chromium and 0.5 per cent of molybdenum may be successfully used in hydrogenation. It is of interest that chromium steels are resistant to hydrogen even with a content of carbon as high as 0.5 per cent.

If the charging stocks to be hydrogenated contain a considerable percentage of sulphur compounds, steels having a larger proportion of chromium and nickel should be employed. Chromium-nickel steels are also very resistant to hydrogen.

Hydrogenation Units

Very little information is available concerning the hydrogenation units operating in the United States, Germany, and other countries. Figure 16 represents a simplified scheme of the process used by the Standard Oil Company of New Jersey and described by Brown and Tilton.³ Liquid feed and fresh hydrogen are separately compressed to 200 atmospheres, mixed and passed through a heat exchange countercurrent to the hydrogenated products moving from the reaction chamber. The preheated oil-hydrogen mixture is heated in a tube heater and passed to the reaction chamber which is filled with a catalyst. After conversion the hydrogenation products go through the above-mentioned heat exchanger and a cooler to a high-pressure separator, where unreacted hydrogen is separated and then recycled to the reaction chamber. The recycle hydrogen is introduced at various points of the reaction chamber, as shown in the figure, to cool the reaction mixture. As has been pointed

out, hydrogenation is accompanied by an evolution of heat and an increase in temperature as the oil-hydrogen mixture passes through the catalyst chamber. The cooling controls the temperature of the process. The liquid hydrogenation products are passed to a lower pressure and stabilized in a conventional manner. Only caustic washing is required for complete finishing.



Courtesy "Oil and Gas Journal"

FIGURE 16.—Flow Chart of the Hydrogenation Process.

As has been mentioned above, mostly narrow fractions are hydrogenated in the units of the Standard Oil Company of New Jersey for the production of aviation fuels, special naphthas, etc., and the process is carried out in a one-stage operation. The daily capacity of each of the two units of the Standard Oil Company of New Jersey is 5000 barrels.

The hydrogenation units operating in Germany process heavy tar distillates in a two-stage operation. Each of the units is composed of two furnaces and two reaction chambers. Each furnace has two parallel coils, one for distillate and one for hydrogen. The distillate is pumped into the first furnace at a pressure 200 atmospheres, where it is heated to 427°C. (800°F.). The hydrogen is heated to the same temperature and under the same pressure in the hydrogen coil. The distillate and the hydrogen, heated to the required temperature, enter the reaction chamber where destructive hydrogenation is then effected. The temperature of the reaction products rises to 455°C. (850°F.) at the outlet of the reaction

chamber. The mixture of synthetic crude and hydrogen passes from the reaction chamber through the heat exchangers and condensers into the separator, where the gases are separated from the synthetic crude. The latter is then distilled into three fractions: gasoline, the intermediate fraction with a boiling range of 175-300°C. (347-572°F.) or somewhat higher, and residue. The residue is recycled to the charging feed, while the intermediate fraction is passed into the second furnace where it is heated to 477°C. (900°F.) under 200 atmospheres pressure. The hydrogen is preheated to the same temperature and under the same pressure in the same furnace. The hydrogen and the distillate then enter the second reaction chamber having the fixed catalyst. The process takes place in vapor phase. As a result, the temperature of the synthetic crude rises to 510°C. (950°F.). From the reaction chamber the synthetic crude and hydrogen are passed through the heat exchangers and condensers into a second separator for separation and further distillation. The synthetic crude is distilled into three fractions as has been described above.

The Italian hydrogenation units have been described by Coppe-Zuccari.⁵ The units, of daily capacity of about 3000 barrels, process the Albanian crude. The crude is first distilled and separated into straight-run gasoline, kerosene, gas oil and residuum. Gas oil is destructively hydrogenated in vapor phase, while the residuum is hydrogenated in the liquid phase process. A part of the hydrogenated residuum is distilled in high vacuum for the production of lubricating distillates and residuum. A light lubricating distillate is passed directly to the dewaxing plant. A heavy lubricating distillate is hydrogenated under moderate temperature conditions and then is passed to the same dewaxing plant. The residuum of the vacuum distillation is solvent-treated and then dewaxed. The Italian hydrogenation units are of interest from the standpoint of wide application of hydrogenation to various fractions of crude.

VARIOUS APPLICATIONS OF HYDROGENATION

The potential applications of hydrogenation are numerous, beginning with the production of gasoline in maximum yields and ending with the improvement of properties of lubricating oils, Diesel fuels, etc. The following applications are to be discussed:

1. Conversion of heavy asphaltic crudes and refinery residues into gasoline and gas oils.
2. Conversion of crudes and gas oils into gasoline and other naphthas.
3. Conversion of low-grade lubricating oils into high-grade lubricating products.
4. Conversion of low-grade burning and Diesel oils into high-grade products.
5. Conversion of unstable and sulphur-containing cracked gasolines into high-grade products.

Conversion of Heavy Crudes and Residues

As has been discussed above, the hydrogenation of heavy crudes and residues may be carried out either in one or two stages. The first stage is the destructive hydrogenation of a heavy charge to gas oil and gasoline. The process is performed at moderate temperatures—about 470°C. (878°F.). No coke or residuum is formed. The yield of gas is moderate—about 10 per cent by weight. As a result, the total yield of gas oil and gasoline amounts to 100 per cent by volume or more. The gas oil produced has a much lower boiling range than the original charge. The asphalt present in the original heavy crude or residuum is converted into oil. The sulphur content is considerably reduced.

The mechanism of this process has been explained above. The heaviest hydrocarbons, resins and asphaltenes are partially hydrogenated and cracked in the hydrogenated ring, forming gas oils. Simultaneously, the oxygen and sulphur of resins and asphaltenes are reduced to water and hydrogen sulphide, resulting in a decrease in the content of oxygen and sulphur. The formation of gasoline is moderate at this stage of the process. The yield of gasoline, however, may be increased *ad libitum*, if the gas oil formed is destructively hydrogenated in the second stage under more severe temperature-time conditions.

The results of destructive hydrogenation of a cracking tar were reported by Haslam and Russell,¹⁰ and are given in Table 103. The yields of gasoline in this operation may be considerably higher, up to 30 per cent or more.

Table 103. Hydrogenation of Cracking Tar.

	Cracking Tar	Hydrogenated Product
Yield of synthetic crude (% by Vol.)		98.9
A.P.I. gravity	12.4	23.5
I.B.P. (°F.)	300	153
Per cent at 650°F.	34.5	67.0
Per cent at 700°F.	49.0	82.0
Per cent sulphur	0.702	0.246
Yield of gasoline on charge (% by Vol.)		14.0
A.P.I. of gasoline		56.4
Per cent sulphur in gasoline		0.019
Yield of gas oil on charge (% by Vol.)		84.9

Haslam and Russell pointed out that the gas oil produced in high yield from heavy crudes and residues can be successfully cracked in conventional cracking units. The cracking residuum formed may be returned to the hydrogenation process. The combined yield of gasoline from heavy residues in hydrogenation and cracking operations would be approximately 100 per cent. The combination of hydrogenation and cracking may be more acceptable from the commercial standpoint due to a wide use of the cheaper cracking process. Other possibilities of the combination of cracking and hydrogenation were suggested by Haslam, Russell, and Asbury.¹¹ For instance, cracking is carried out in a once-through operation. The recycle stock is then destructively hydrogenated also in a

once-through operation, forming gasoline and hydrogenated recycle stock of lower boiling range and specific gravity than the cracked recycle stock used. This improved recycle gas oil can be run in the cracking coils with better results than the cracking recycle stock with respect to the yield of gasoline.

Conversion of Gas Oils into Gasoline

The conversion of gas oils into gasoline can be carried out at moderate and at high temperatures. The first process is performed at temperatures of 400-450°C. (752-842°F.) or somewhat higher, and the second at 500-560°C. (932-1040°F.). Gasoline and gas are the final products of the process, which is carried out in vapor phase in the presence of various catalysts.

The results of moderate and high-temperature hydrogenation are predetermined by the temperature of the process and by the catalysts. At moderate temperatures the reactions of hydrogenation take place more readily, and the resulting gasolines are more paraffinic and of comparatively low octane number. The naphthenic gasolines of higher octane number may be produced from selected, highly naphthenic gas oils. Gas formation is not great, due to the moderate cracking conditions.

At high temperatures the hydrogenation reactions occur mostly as intermediate reactions of equations 29-31, leading to the formation of derivatives of benzene as the final products of destructive hydrogenation of cyclic hydrocarbons. Thus naphthenic gas oils are frequently employed for high-temperature hydrogenation. Gas formation is large, due to the severe conditions of the process. The gasolines formed are highly aromatic and antiknocking. Because of the small proportion of paraffins and naphthenes in gasolines, the relative amount of lower boiling fractions is small and deficient.

The catalysts are the second factor affecting the results of the processes in question. According to Pier,²² they may be classified as follows:

1. Those which are very active in hydrogenation and cracking (A).
2. Those moderately active in hydrogenation and very active in cracking (B and C).
3. Those used in high-temperature hydrogenation above 500°C. (932°F.) (D).

Very active hydrogenation catalysts produce high yields of gasoline of low octane number. More naphthenic and aromatic gasolines of higher octane number are produced in the presence of less active hydrogenation catalysts, or at high temperatures. The properties of gasolines produced from the same mixed base gas oil in the presence of different catalysts are given as follows:

Catalyst	A	B	C	D
Specific Gravity	0.716	0.722	0.730	0.787
Octane Number				
Research Method	57	69	72	80
Motor Method	58	69	70	74

It is understood that not only gas oils but also heavy crudes and residues can be destructively hydrogenated to gasoline. The hydrogenation of heavy residues is carried out in two stages, the first of which corresponds to the operation described in the previous section. The gas oil formed in the first stage is then hydrogenated in vapor phase either at moderate or at high temperature.

In the moderate temperature process very high yields of gasoline are obtained, up to 110 per cent by volume or higher. The formation of gas is correspondingly small, not exceeding 10-15 per cent by weight. According to Haslam *et al.*,¹¹ the yields of gasoline do not depend markedly on the A.P.I. gravity of the gas oils. For example, a light hydrogenated gas oil of A.P.I. gravity 32.1 and a cracked Coastal gas oil of A.P.I. gravity 21.5 give very close yields of gasoline, 113 and 110.6 per cent by volume, respectively.

The data on moderate-temperature destructive hydrogenation from the article by Sweeney and Voorhees²⁷ are summarized in Table 104. The

Table 104. Moderate-Temperature Destructive Hydrogenation.

	Mixed Virgin and Cracked Gas Oil	Heavily Cracked Gas Oil
Charging Stock		
Gravity (A.P.I., 60°F.)	25.1	21.5
Specific Gravity (60°F.)	0.9036	0.9248
5% Point (°F.)	448	440
50% Point (°F.)	536	471
Final B.P. (°F.)	684	565
Sulphur (%)	0.864	0.500
Fresh Feed (%)	60	60
Gasoline		
Yield (% by volume)	116	122
Gravity (A.P.I., 60°F.)	66.1	58.9
Specific Gravity (60°F.)	0.7161	0.7432
% at 212°F.	39.5	29.5
Final B.P. (°F.)	374	416
Sulphur (%)	<0.02	<0.02
Octane No. (CFR-Motor Method)	60.4	58.7

gasolines produced in this operation are of high A.P.I. gravity (about 60 or higher), rich in lower boiling fractions (30-40 per cent and more to 212°F. in A.S.T.M. distillation), stable, and low in sulphur. The octane number, however, is low, close to 60 by the Motor Method.

A modification of moderate-temperature destructive hydrogenation described by Murphree *et al.*¹⁸ is the processing of selective highly naphthenic and aromatic virgin and cracked gas oils over newly developed catalysts. The process is performed at moderate temperatures, about 400-450°C. (752-842°F.). The conversion per pass is as high as 60-70 per cent and the final yields of 80 to 90 per cent by volume, if aviation fuel is manufactured. This method produces gasolines of comparatively high octane number—about 75—and of satisfactory lead susceptibility. This method of operation is recommended for the production of aviation gasolines which are almost as stable as straight-run products. When leaded, the gasolines have octane numbers of 90 or more. The data of

Brown and Gohr² on this type of destructive hydrogenation are given in Table 105.

Table 105. Moderate-Temperature Destructive Hydrogenation of Various Stocks.

	Heavy Naphtha Coastal	Venezuel. Kerosene	Crude Venezuelan	Recycle Stock Mirando	Stock W. Texas
Charging Stock					
Gravity (A.P.I., 60°F.)	32.9	36.1	31.0	26.1	31.8
Specific gravity (60°F.)	0.8607	0.8443	0.8708	0.8978	0.8665
Aniline point (°C.)		56	39	27	38
Sulphur (%)	0.051	0.09	0.39	0.06	0.68
I.B.P. (°F.)	280	326	316	211	238
50% point (°F.)	424	425	450	465	451
F.B.P. (°F.)	564	533	544	572	601
Hydrogenated Aviation Fuel					
Gravity (A.P.I., 60°F.)	64.9	67.1	65.9	62	61.8
F.B.P. (°F.)	278	295	290	268	278
Acid heat (°F.)	2	2	3	3	2
Color, Saybolt	+30	+30	+30	+30	+30
Copper dish gum (mgs./100 cc.)	2				
Induction period (min.)	1500+				
Sulphur (%)	0.007				
Octane No., CFR-Motor Method, Clear	78.3	76.6	76.0	76.8	75.3
+2.5 cc. T.E.L.		90.0	88.4		
+3.5 cc. T.E.L.				90.8	90.4

High-temperature destructive hydrogenation at 500-560°C. (932-1040°F.) produces lower yields of gasoline, about 90 per cent by volume, at the expense of greater gas formation. The gas formation amounts to 25 per cent by weight or more. The yield of aviation gasolines is from 58 to 71 per cent. The gasolines are of low A.P.I. gravity (about 45 or lower) and are deficient in lower boiling fractions. The cut to 212°F. is close to 20 per cent. The sulphur content and gum formation are as small as those of gasolines hydrogenated at moderate temperatures. The octane number of gasoline hydrogenated at high temperature is comparatively high (about 80) due to a high content of aromatic hydrocarbons; it depends on the charging stock, as well as on the catalyst. According to Haslam, Russell and Asbury, the octane number of gasolines hydrogenated at high-temperature from the same charging stock varies from 72 to 85, depending on the catalyst. The response of these gasolines to tetraethyl lead, however, is comparatively poor. The examples from the

Table 106. High-Temperature Destructive Hydrogenation.

	Tops from Kerosene Edeleanu Extract	Total Edeleanu Extract	West Texas Cracked Recycle Stock
Charging Stock			
Gravity (A.P.I., 60°F.)	34.2	25.3	32.6
Specific Gravity (60°F.)	0.8540	0.9024	0.8623
I.B.P. (°F.)	294	326	166
50% Point (°F.)	369	441	405
F.B.P. (°F.)	469	555	523
Operating Conditions			
Total Feed/Cat. Vol./Hour*	1.5	1.5	1.0
Vol. % of Fresh Feed	63	71	55
Aviation Fuel			
Yield (unstabil.) (% by vol.)	77	60	64
Color, Saybolt	+30	+27	+25
Copper Dish Gum (mgs./100 cc.)	5	4	2
Induction Period (min.)	690	930	510
Acid Heat (°F.)	10	9	14
Octane No., ASTM Motor Method	84.0	86.8	81.2

* Volume of total feed per volume of catalyst per hour.

cited article given in Table 106 illustrate the results of high-temperature hydrogenation.

The aromaticity and octane numbers of the fractions of high-temperature hydrogenation gasolines increase with increasing boiling range, as is evident from the data of Table 107.

Table 107. Octane Numbers of Fractions of a High-Temperature Hydrogenation Gasoline.

Cut No.	%	50% Boiling Point (°F.)	—Octane Number— (Army Method)	
			Clear	+3 cc. T.E.L.
1	0-20	164	78	93.5
2	20-40	222	83	94.0
3	40-60	253	91.5	98.5
4	60-80	276	94	100
5	80-90	289	94	100

Due to the uncommon properties of hydrogenated gasolines obtained at high temperatures, the gasolines may be used for the manufacture of special products, such as high-flash safety aviation fuels or aromatic naphthas.

The total gasoline fraction of aromatic gasoline produced by high-temperature hydrogenation is distilled into two fractions, below and above 160°C. (320°F.). The overhead fraction and the bottoms represent light aviation and high-flash safety aviation fuels. The properties of these fuels are given in Table 108.

Table 108. Production of High-Flash Safety Aviation Fuel.

Feed Stock: A.P.I. Gravity 25.5, Sulphur 0.89%, I.B.P. 348°F, F.B.P. 570°F.

	—Hydrogenated Products—	
	Light Aviation Fuel	High-Flash Safety Aviation Fuel
Yield on feed (% by vol.)	29.0	55.0
Gravity (A.P.I., 60°F.)	49.5	28.5
Abel flash (°F.)		107
Color, Saybolt	30	28
Copper dish gum (mgs./100 cc.)	2.5	4.8
Doctor test	Passes	Passes
Corrosion test	Passes	Passes
Aniline point (°F.)		-20
I.B.P.	100	309
F.B.P.	335	411
Octane no.	83	93

Another application of the aromatic gasolines hydrogenated at high-temperature is the production of solvent naphthas of high solvency and aromaticity. Sweeney and Tilton²⁶ obtained four fractions boiling in the range 200-460°F. from aromatic hydrogenated gasoline and described the properties of the naphthas produced. The summarized results are given in Table 109.

The aromaticity and solvent power of the hydrogenation naphthas increase with the boiling range. The properties are close to those of highly refined coal-tar solvents. Hydrogenation solvent naphthas are commercially manufactured by Standard Oil Company of New Jersey.

Table 109. Properties of Solvent Naphthas Produced by Hydrogenation.

Boiling range (°F.)	Gravity, 60°F. A.P.I.	Specific Gravity	Aniline point (°F.)	Color Say-bolt	Sulphur (%)	Flash (°F.)	De-methyl Sulphate Value	Dilution Ratio	Kauri Butanol No.	Evaporation Rate (Hart Balance) 100% (min.)
200-275	50.6	0.777	52	+25	0.038	60	24	1.9	55.2	4.25
275-365	34.0	0.855	-1	+23	0.040	61	62	2.8	75.6	21.25
365-419	26.2	0.897	-10	+23	0.040	135	187	2.6	77.3	80
419-460	19.6	0.937	-33	0	0.042	190	100	2.4	85.7	

Note: Doctor and corrosion tests are satisfactory; odor sweet and slightly aromatic.

Haslam, Russell and Asbury¹¹ have given very comprehensive comparative data on the results of simple cracking and both types of destructive hydrogenation at moderate (M.T. Hydr.) and high temperatures (H.T. Hydr.) obtained in commercial operation in a 15,000-bbl. per day Tube-and-Tank unit and in a 5,000-bbl. per day hydrogenation plant. These data are given in Table 110.

Table 110. Comparison of Hydrogenation and Cracking.

Feed stock A.P.I. gravity 50% at °F. Aniline point	Mixed Crack Stock			Coastal Recycle Oil			Heavy Naphtha Btms.		
	28.4 453 90			26 556 125			30.8 447 110		
	H.T. M.T.			H.T. M.T.			H.T. M.T.		
Operation	Crack	Hydr.	Hydr.	Crack	Hydr.	Hydr.	Crack	Hydr.	Hydr.
Total throughput (vol./cat. vol./hr.)	...	4.2	2.2	...	4.0	2.2	...	4.0	2.2
Cracking (bbls./day)	15,000	15,000	15,000
Vol. % fresh feed	31.5	46.0	72	38	42	67	32.0	59.0	76.0
Vol. % 12 tar. on fresh feed	42.0	None	None	49.5	None	None	38.5	None	None
Vol. % raw 420°F. E.P. gasoline on fresh feed	50.5	93.0	110.0	44.0	92.6	110.0	54.5	91.0	109.0
Vol. % finished gasoline	47.0	89.5	109.5	41.0	88.5	109.5	50.5	87.5	108.5
Octane No. of finished gasoline	78.5	74.0	64.0	72.2	67.0	58.0	75.5	69.0	60.0
Feed stock A.P.I. gravity 50% at °F. Aniline point				M.C. Gas Oil 40.7 440 146			M.C. Gas Oil 33.4 540 156		
				H.T. M.T.			H.T. M.T.		
				Hydr. Hydr.			Hydr. Hydr.		
Operation	Crack	Hydr.	Hydr.	Crack	Hydr.	Hydr.	Crack	Hydr.	Hydr.
Total throughput (vol./cat. vol./hr.)	...	4.0	2.2	...	4.0	2.2	...	4.0	2.2
Cracking (bbls./day)	15,000	15,000	15,000
Vol. % fresh feed	43.5	76.0	81.0	43.5	76.0	81.0	35.0	55.0	70.0
Vol. % 12 tar. on fresh feed	15.0	None	None	15.0	None	None	29.5	None	None
Vol. % raw 420°F. E.P. gasoline on fresh feed	72.5	89.0	108.0	72.5	89.0	108.0	61.5	91.0	109.0
Vol. % finished gasoline	67.5	85.5	107.5	67.5	85.5	107.5	57.0	87.5	108.5
Octane no. of finished gasoline	68.2	64.0	57.0	68.2	64.0	57.0	69.6	63.0	54.0

Note: Octane numbers were determined on Series 30 Ethyl Gasoline Corporation motor at 212°F. and 600 RPM.

The difference in gasoline yields between hydrogenation and cracking is much more significant for heavy recycle stocks. From these stocks the yields of gasoline in hydrogenation are approximately doubled in comparison with cracking. The octane numbers of cracked gasolines are invariably higher than those of hydrogenated products from the same charging stock. This result is not unexpected. The simple cracking produces more aromatics and olefins that are partially (olefins completely) hydrogenated to hydroaromatics and paraffins in destructive hydrogenation. As a result, the octane numbers decrease, particularly in the moderate-temperature process.

Conversion of Low-grade Lubricating Distillates

The conversion of low-grade lubricating distillates into high-grade products can be performed at low and moderate temperatures, about 400°C. (752°F.) or somewhat higher. Hydrogenation under these conditions transforms aromatics into partially hydrogenated hydrocarbons, resulting in the increase of A.P.I. gravity and viscosity index. The resins and asphaltic constituents are hydrogenated to hydrocarbons with splitting of sulphur, resulting in improvement of the color, Conradson carbon value and content of sulphur. From 80 to 90 per cent of the sulphur in the charging stock is eliminated after hydrogenation. On the other hand, in addition to hydrogenation, some decomposition reactions take place simultaneously, forming hydrocarbons of low molecular weight. The partial splitting of very long paraffinic side chains is responsible for a considerable reduction in the viscosity of lubricating distillates treated. A part of the original viscous oils is transformed into light gas oil, and even into gasoline. Thus the original raw lubricating distillate produces a lubricating oil of better viscosity index, color and Conradson carbon test, but of lower viscosity. The yield of the hydrogenated lubricating oil is around 70 per cent of the original lubdistillate at the expense of the gas oil and naphtha formed. The process has been described by Haslam and Russell.¹⁰

A lubricating distillate from Winkler crude of the following properties:

A.P.I. gravity	20.1
Viscosity at 100°F.	690
Viscosity at 210°F.	62
Viscosity index	32
Pour point (°F.)	0
Flash (°F.)	420
Carbon (%)	0.410

was non-destructively hydrogenated, forming 105 per cent by volume of the hydrogenated product of A.P.I. gravity 30.1. The steam distillation of this product gave about 6 per cent gasoline, 26 per cent gas oil and 72 per cent luboil of the following properties:

A.P.I. gravity	27.5
Viscosity at 100°F.	286
Viscosity at 210°F.	50
Viscosity index	83
Flash point (°F.)	410
Pour point (°F.)	0
Carbon (%)	0.015

Another very viscous Midcontinent lube distillate of the properties:

A.P.I. gravity	22.0
Viscosity at 100°F.	3100
Viscosity at 210°F.	144
Viscosity index	72
Carbon	3.31

gave, in addition to 25 per cent gas oil and gasoline, 67.5 per cent dewaxed neutral of the following properties:

A.P.I. viscosity	29.2
Viscosity at 100°F.	580
Viscosity at 210°F.	68.7
Viscosity index	101
Carbon	0.13

The data given above show that the decrease in viscosity of hydrogenated lubricants is very substantial, particularly for the more viscous oils.

Conversion of Low-grade Burning and Diesel Oils

The burning properties of kerosene and the ignition characteristics of Diesel oils (cetane number) depend on the paraffinicity of oils. A high content of aromatic and unsaturated hydrocarbons is equally detrimental to both burning and Diesel oils, resulting in poor quality. The hydrogenation of low-grade burning and Diesel oils under moderate temperature conditions transforms aromatic and unsaturated hydrocarbons into hydroaromatics and paraffins, increasing the paraffinicity of oils. Sulphur compounds, as well as resins, if present, are reduced to hydrocarbons. The process is also accompanied by some decomposition reactions, forming hydrocarbons of low molecular weight. As a result, the fractional composition and viscosity of hydrogenated products are changed as compared with the charging stocks. From the commercial standpoint, the results are more favorable than in the case of lubricating oils, since the decrease in viscosity and a lighter fractional composition are rather beneficial to the final products. Some data of Haslam and Russell¹⁰ illustrate the results of hydrogenation of burning oil distillates (Table 111). The term 400 viscosity oil is used to denote the fraction of about 400 viscosity at 60°F. and above 100°F. Abel flash.

Table 111. Hydrogenation of Various Burning Oil Distillates.

	Low-Grade Midcontinent	Long Beach, California	Cracked Midcontinent
Charging stock			
A.P.I. gravity	40.2	36.8	39.7
Viscosity at 60°F.	485	750	400
Sulphur (%)	0.221	0.240	0.334
% 400 vis. oil in original	58	40	100
A.P.I. gravity of 400 vis. oil	41.2	39.9	39.7
Viscosity of 400 vis. oil	400	400	400
Hydrogenated product			
Yield (% by vol.)	106	99	103
A.P.I. gravity of total product	48.9	45.6	47.2
Sulphur (%) of total product	0.006	0.025	0.014
% 400 vis. oil in total product	83	60	80
A.P.I. Gravity of 400 vis. fraction	46	43.3	44.4
Viscosity of 400 vis. fraction	415	400	360
Sulphur (%) in 400 vis. fraction	0.007	0.012	0.025
Flash (°F.) Abel	107	120	106
Color	22	25	25
% Sulphur eliminated	97	90	96
Improvement in A.P.I. of 400 vis. fraction	4.8	3.4	4.7

An almost total elimination of sulphur should be mentioned. The sulphur compounds are very unstable under the conditions of hydrogenation, being transformed into hydrocarbons and hydrogen sulphide.

The same results are obtained for the processing of Diesel oils. For instance, a very heavy Venezuelan distillate of A.P.I. gravity 18.5 was

hydrogenated, and produced 20.5 per cent of gasoline and 87.8 per cent of Diesel oil, the properties of which were:

A.P.I. gravity	35.0
Aniline point (°F.)	188
Diesel index	66
Color	+22
Sulphur (%)	0.02

Another example of the production of an excellent Diesel fuel from an aromatic and phenolic oil from the article of Pier²¹ is given in Table 112.

Table 112. Hydrogenation of Aromatic Oil to Diesel Fuel.

	Original Oil	Hydrogenated Oil
Specific Gravity at 20°C.	0.990	0.881
Phenols (%)	22	0.3
End point (°C.)	354	337
Aniline point (°C.)	8	56
Cetane number	0	60
Pour point (°C.)		-18

Vlugter, Waterman and van Westen^{31a} hydrogenated non-destructively various gas oils (Diesel fuels) with the following results:

	Straight-run				Cracked	
	Origin.	Hydrog.	Origin.	Hydrog.	Origin.	Hydrog.
D ₄ ^{2.0}	0.9004	0.8630	0.8801	0.8320	0.8632	0.8192
Aniline point	42.0	63.6	63.5	80.6	52.0	78.4
Cetene no.	37	49	53	68	61	79
Cetane no.	32	43	46	59	53	69
% by wt. of olefins	16	..
% by wt. of arom. rings	28	7	20	3	20	2
% by wt. of naphth. rings	30	45	17	29	13	26
% by wt. of paraff. side chains	42	48	63	68	67	72

Thus the hydrogenation of gas oils increases the cetane numbers by 10 units or more.

Conversion of Unstable and Sulphur Containing Gasolines

The unstable gum-forming unsaturated hydrocarbons of unrefined cracked gasolines are easily converted into saturated hydrocarbons by hydrogenation under mild processing conditions. The sulphur compounds are reduced to hydrocarbons, forming hydrogen sulphide. The removal of sulphur may be almost complete, if the temperature of the process is around 400°C. (725°F.) or higher. The results of hydrogenation of an unrefined cracked gasoline, reported by Haslam and Russell,¹⁰ are given in Table 113. As can be seen from Table 113, the hydrogenation of naphtha is accompanied by a certain decomposition, resulting in a lighter fractional composition of the hydrogenated gasoline.

Hydrogenation of low-octane straight-run and cracked naphthas under more severe conditions produces reformed and refined gasolines. This process is designated as hydrotreating. As in the case of thermal reforming, the reforming effect depends mostly upon the temperature-time

Table 113. Hydrogenation of Cracked Naphtha.

	Original Cracked Smackover Naphtha	Hydrogenated Product, 100% Yield
Total Product		
A.P.I. gravity	46.4	51.9
Sulphur (%)	0.395	0.019
Doctor test	Positive	Negative
Color	Straw	+25
Per Cent at 212°F.	14.5	12.0
Per Cent at 302°F.	40.5	45.0
Per Cent at 374°F.	64.0	73.5
Per Cent at 400°F.	71.5	82.0
F.B.P. (°F.)	540	502
Gasoline		
A.P.I. gravity	53.9	55.3
Sulphur (%)	0.188	0.006
Porcelain dish gum (mgs./100 cc.)	12	1
Copper dish gum (mgs./100 cc.)	21	4

conditions. The increase in octane number is accompanied by the refining effect of hydrogen, resulting in desulphurization and hydrogenation of unstable hydrocarbons. No data are so far available on the conditions of hydrotreating and the properties of hydrotreated gasolines.

Economics of Hydrogenation

At the present time, at low crude and gasoline prices, the economic position of the hydrogenation process is unfavorable. The high yields of hydrogenation gasoline as compared with those of conventional cracking are more than counterbalanced by the high investment and operation costs of hydrogenation. According to Haslam, Russell and Asbury,¹¹ the additional investment in moderate-temperature hydrogenation over cracking averages about \$257 per barrel per day of gasoline capacity. For high-temperature hydrogenation the additional investment over cracking is still higher, ranging from \$430 to \$650 per barrel per day of gasoline capacity. The figures given cover the complete investment expenses for both hydrogenation and cracking, including steam generation, water pumping, acid treating, rerunning, doctor sweetening, acid recovery, as well as site-preparation. On the other hand, the operation expenses of hydrogenation are much greater than in the case of cracking due to the higher pressures, the use and recycling of hydrogen, the use of catalysts, etc.

Also, the octane numbers of hydrogenation gasolines are mostly lower than in the case of cracking, if the same charging stock is used in both operations. In other words, hydrogenation does not offer any advantage with respect to the largest and most essential use of gasolines, *i.e.*, as automobile and aviation fuels.

Other possible applications of hydrogenation discussed in this chapter such as, for instance, improvement of the qualities of lubricating oils and other products, production of high solvency naphthas, etc., do not improve the economics of the process. The same results may be obtained

by other commercially available and cheaper methods, for instance, by solvent refining and by high-temperature vapor-phase cracking.

The economic position of hydrogenation, however, may be entirely different at higher prices for crudes and gasolines. Haslam *et al.* state that "at gasoline prices of 7-9 cents per gallon hydrogenation appears attractive on practically all stocks."

The present large-scale industrial development of hydrogenation in Germany, England and Italy is subsidized by the elimination of taxes on the hydrogenated fuels and by other similar measures protecting the manufacture of gasoline from coal and various tars. Even under these conditions, the process is not very attractive commercially. According to Gordon,⁶ the cost of production of a gallon of hydrogenation gasoline in England is about 13 cents. The recent Viscount Falmouth and Labor Party reports estimate the cost of hydrogenation gasoline from coal to be about 11-11.5d per Imperial gallon, or about 10 cents per U. S. gallon.^{5b}

At present the total production of hydrogenated gasoline in Germany is close to 12,000,000 barrels a year, in England about 1,300,000 barrels a year and in Italy about 1,800,000 barrels a year.

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Chapter 4

Cracking Equipment

BASIC PRINCIPLES

This chapter relates to the equipment necessary for the conventional cracking processes used for treating liquid charging stocks. Other processes, such as catalytic cracking or thermal conversion of gases, employ the same conventional equipment with certain specific apparatus of special design. These processes have been described in Chapter 2.

The design of the cracking plant equipment is based upon the fundamental factors of cracking discussed in Chapter 2, which may be summarized as follows. The formation of cracked gasoline from charge begins as soon as the required temperature is reached. The velocity of its formation increases with increasing temperature, doubling for every 14°C. (25°F.) in the pressure process, and for every 18°C. (33°F.) in the vapor-phase process. The velocity at a given temperature depends upon the nature of the charge, being greater for the products of high boiling range and high paraffinicity and *vice versa*. The pressure does not appreciably affect the rate of formation of gasoline.

On the other hand, the formation of coke starts after a certain interval of time after the cracking process has begun. For most of the straight-run distillates, coke formation begins after 25 to 30 per cent of cracked gasoline has been obtained, and for recycle stocks after approximately 20 per cent has been obtained. For heavy crudes and residues the yield of gasoline corresponding to the beginning of coke formation is still lower—about 10-15 per cent. As a result of this difference in the kinetics of gasoline and coke formation, it becomes possible to process the charge at a temperature which causes a sufficient rate of cracking without producing coke. The allowable crack-per-pass, or the maximal yield of gasoline without forming coke, equals approximately 20 per cent for the recycle operation in the mixed-phase process. The allowable crack-per-pass in the vapor-phase process is only 10 per cent.

Higher yields of gasoline per pass are allowable in destructive hydrogenation due to the elimination of coke formation. The yields per pass in this process may be as high as 60 per cent. In catalytic cracking the yields per pass amount to 40 per cent, owing to the deposition of coke on the catalyst. In contradistinction to thermal residuum cracking, catalytic cracking is accompanied by appreciable coke formation (page 146). The yields of gasoline per pass in the thermal conversion of gases

are from 5 to 15 per cent by weight. At higher yields per pass the gas formation and condensation reactions decrease considerably the final yields of gasoline (Chapter 2, Table 63).

In thermal cracking, high yields of cracked gasoline from gas oils (up to 60-70 per cent) may be obtained only as a result of the recycling operation. The gasoline and the heavy condensation products formed per pass are separated in special parts of the cracking equipment from the intermediate distillates which are cracked repeatedly in the recycle operation, either alone or mixed with fresh charge.

The allowable crack-per-pass that can be obtained without appreciable coke formation predetermines the optimum operation of a cracking unit. It is evident that a high crack-per-pass corresponds to a minimum recycle ratio, and *vice versa*. On the other hand, a low recycle ratio means a relatively small amount of material to be heated, pumped, cracked and fractionated; in other words, low first costs and low operation costs. In addition, a cracked gasoline of higher octane number is obtained with a higher crack-per-pass.

Cracking fresh charge and recycle stock in one operation does not produce the best results with reference to yields per pass, final yields and octane numbers. Better results are obtained by selective cracking, in which various fractions separated from fresh and recycle stocks are cracked under selective conditions of temperature, time and pressure (page 137).

The temperature-time conditions of cracking depend upon the nature of the charging stocks. Lower boiling products can be cracked under more drastic conditions than can high-boiling or residual stocks, without appreciable coke formation. There is a definite tendency toward the use of high temperatures, due to the higher efficiency of cracking units under these conditions, as well as toward higher octane numbers of gasolines produced under drastic processing conditions.

When cracking light gas oil in the mixed-phase process, the temperature of cracking is up to 500-550°C. (932-1022°F.) depending mostly upon the fractional composition of the charging gas oil. The temperature of reforming heavy naphthas is close to the figures given above. The temperature of the vapor-phase cracking of gas oils is still higher, up to 550-600°C. (1022-1112°F.). The cracking temperature of straight-run residues in the mixed-phase process is much lower, not exceeding 480°C. (896°F.).

The main factors in cracking are temperature, time, and the individual characteristics of the charge. The pressure is of secondary importance, varying from 50 lbs. per sq. inch gauge in vapor-phase cracking units to 1500 lbs. in some Tube and Tank units. This fact alone indicates that the pressure is not one of the basic factors in cracking. The use of high pressures is beneficial from the standpoint of heat transfer, avoidance of local overheating, and compactness of cracking equipment. These secondary factors, however, are commercially very vital, and are re-

sponsible for the unquestionable predominance of pressure-cracking over the vapor-phase process.

General Arrangement of Cracking Equipment

The charging stock, which is first preheated in heat exchangers or by direct heat exchange in a fractionating column, is frequently mixed with recycle stock; it then enters the cracking coil where it is heated to the cracking temperature. Further cracking to a required extent, predetermined by the allowable crack-per-pass, may be accomplished either in soaking tubes or in a reaction chamber connected with the coil. The pressure in the reaction chamber is the same as in the outlet from the coil.

The arrangement of the cracking equipment, designed for separation of the synthetic crude formed, is different in cracking units using evaporation at low pressures from that in units maintaining the same pressure in all subsequent operations, and in all other parts of the equipment.

In the soaking tubes, as well as in the comparatively small reaction chambers of Cross or Tube and Tank units, there occurs no separation of residuum and distillates from the synthetic crude formed, and the total synthetic crude passes through a reduction valve into an evaporator. In the evaporator, separation of distillates from heavy cracked residuum is effected at a low pressure. The residuum is removed from the evaporator. The distillates leave the evaporator and enter the fractionating tower, from which a gasoline or pressure distillates of required end point, as well as a recycle stock, are obtained. The recycle stock is mixed with fresh charge and the mixture is pumped to the heater for cracking.

In the Dubbs or Holmes-Manley process, separation of the synthetic crude formed into distillates and heavy residuum takes place in large reaction chambers under the operating pressure. The distillates enter the fractionating column for the separation of gasoline or pressure distillate from recycle stock. Separation, as well as condensation of the pressure distillate, is performed under the same operating pressure. The mixture of recycle stock and fresh feed is pumped to the cracking coil.

In both types of cracking systems, the residuum is not properly separated from the low-boiling distillates owing to the lack of fractionation in the evaporator or reaction chamber. For this reason, the residuum is flashed in a special chamber, to separate the heavy tar or final cracked residuum from the distillates which can be recycled.

Cracking Coils

As has been mentioned above, the charge is heated in the tube still to a temperature which secures a sufficient rate of cracking. The temperature of the charging stock entering the cracking tube still is customarily from 300 to 350°C. (572-662°F.). In the cracking coil the temperature of the charging stock is gradually raised to the outlet temperature from 480 to 550°C. (896-1022°F.) in the mixed-phase process, or to 550-600°C. (1022-1112°F.) in the vapor-phase process.

The charge is kept at the cracking temperature for the required time. This stage, soaking, takes place either in soaking tubes or in a special reaction chamber (soaker). The soaking tubes may be arranged either in the same tube heater as the preheating tubes, or in a separate heater. In some cases, when the final temperature of charge is very high, the length of the soaking tubes and the soaking time may be very short.

In view of the high temperatures and high cracking rates used in modern units, there is no need for a reaction chamber, in which the product is held back for a considerable time under cracking conditions.

The gradual development of cracking heaters and coils is of interest. The first cracking units consisted of a single reaction chamber heated directly to cracking temperature. The next stage was to provide the reaction chamber with parallel tubes for heating the charge. Then the parallel tubes were replaced by a continuous tube-still heater connected with the reaction chamber. Approximately one-half of the cracking took place in the soaking tubes of the heater. At the present time the reaction chambers have been entirely replaced by soaking sections of tubes adapted for the required extent of cracking. The Winkler-Koch Engineering Company was the pioneer of commercial cracking without reaction chambers in this country.

The reaction chambers, however, can be useful for more advanced forms of cracking which are accompanied by some coke formation. The coke formed in cracking gradually fills up the chamber. The reaction chambers are employed in catalytic cracking, as well as in hydrogenation.

The velocity of the charging stock in tubes is of primary importance. The movement of the oil must be turbulent to ensure a high rate of heat transfer. On the other hand, the turbulent movement protects the surface of the tubes from the deposition of carbonaceous materials if they are formed as a result of cracking. A linear "cold" (at 60°F.) velocity of charging stock of 1.5 meters or 5 feet per second is sufficient to ensure a turbulent movement. This figure should be considered rather as a lower limit of the allowable velocity for modern heaters using the high rates of heat transfer. When heavy residual stocks are cracked, the cold velocity must be 6 to 8 feet per second. Velocities as high as 3 meters, or 9.8 feet, per second are used in some modern cracking furnaces. The actual "hot" velocity is, of course, much higher, particularly in hot sections of tubes, owing to the vaporization of at least a part of the charge.

In addition to the high rate of heat transfer, greater crack per pass can be obtained by using high velocities of the charge.

Velocities above 10 feet per second cannot be used in commercial processes due to a very high pressure drop caused by high velocities. It should be kept in mind that the increase in the pressure drop is proportional to the square of the increase in the velocity.

According to Cambron and Bayley,⁵ a high degree of turbulence in vapor-phase cracking is of paramount importance. They cracked a gas oil at temperatures of 600-800°C. in open and in baffled tubes. There

was a marked increase in the yield of gasoline in the baffled tubes, which produced highly turbulent flow. At 600°C. and 650°C. the yields of 205°C. end point gasoline were 8.4 and 16.1 per cent respectively, when an empty tube was used. When a baffled tube was employed, the yields increased to 16.0 and 22.4 per cent respectively, other conditions being the same. At very high temperatures (800°C.) the effect of the baffling on the gasoline yields was negligible, but the content of benzene and toluene in the gasoline was much greater in the baffled tubes. In earlier publications the authors cited⁶ have shown that the yields of olefins and aromatics were greater in the pyrolysis of hydrocarbon gases in the baffled tubes as compared with the open tubes. In addition to the higher yields, vapor-phase cracking or thermal conversion of gases can be carried out in baffled tubes at higher space velocities due to the increased rate of heat transfer.

The capacity of the cracking coil depends upon the diameter of the tubes and the velocity of the charge. A unit treating about 3000 barrels of combined charge (fresh and recycle stock) per day usually has tubes of 2½ to 3 inches I.D. For a daily capacity of 6000 barrels the internal diameter is from 3 to 3½ inches. Large units of the capacity of 10,000 to 12,000 barrels per day have either two parallel coils of 3-3½ inch tubes or one coil of 4-4½ inch tubes. Parallel tubes of small diameter are preferable to one large tube due to the larger heating surface of the smaller tubes.

In some cracking units having two parallel coils in the convection section, the radiant section has only one coil, the diameter of which is the same or a little larger than that of the convection coil. In this way very rapid movement of the oil is created in the tubes exposed to the highest temperature.

Modern cracking furnaces extensively use the radiant heat of the flame of burners. The large surface of radiant tubes readily absorbs the heat of radiation and controls the temperature of the combustion chamber, as well as the heat transfer to radiant tubes. Other means of controlling furnace temperature, widely employed in the past, such as a large excess of air or recirculation of flue gases, are not used in modern furnaces. The part of the radiant heat input is as high as 60 to 80 per cent of the total. As a result, the radiant sections of modern tube heaters are largely developed at the expense of the convection sections. In the convection sections the cracking stock is merely preheated before the main heat input in the radiant sections.

According to Rickerman, Lobo and Baker,²⁸ the safe heat transfer rates in the radiant sections of cracking stills are up to 13,000 B.t.u. per square foot per hour (33,500 Cal. per square meter per hour) of external surface for gas oils, and up to 10,000 B.t.u. for black oils. These figures seem to be rather conservative. According to Mekler,²² much higher heat transfer rates, up to 15,000-20,000 B.t.u. (37,500-50,000 Cal.), are used in some heaters. The higher rates of heat transfer may be used

particularly for the sections of tubes where cracking takes place only to a small extent. In the soaking tubes the rates of heat transfer must be moderate, below 10,000 B.t.u. per sq. inch per hour (25,000 Cal. per sq. meter per hour), to prevent coke formation in more advanced stages of cracking.

The heat transfer rates in the convection section vary from 2 to 4 B.t.u. per sq. foot per hour per Fahrenheit degree of the mean log temperature difference of the flue gases and the outside tube temperature (from 5 to 10 Cal. per sq. meter per hour per centigrade degree of the same log temperature difference). In addition to this purely convective heat transfer, the convection tubes receive radiation heat from the hot flue gases passing through the tubes. The total transfer rate in the convection section varies approximately between 4 and 8 B.t.u., depending on the velocity of flue gases, the size of tubes and the temperature.²²

The first rows of convection tubes have an additional source of radiation heat from the brickwork opposite the tubes. The total heat transfer in the first row of convection tubes may be as high as 15,000-18,000 B.t.u. per sq. foot per hour (37,500-45,000 Cal. per sq. meter per hour). The total heat transfer in other rows of convection tubes is considerably lower, from 8000 to 3000 B.t.u. (20,000 to 7,500 cal.), depending upon the location of the tubes in the convection chamber. The average heat transfer in the convection sections is usually close to 4000-5000 B.t.u. per hour per sq. foot.

In some furnaces the tubes, particularly in the convection section, have cast-iron corrugated elements or gill rings to increase the surface and the heat transfer. The use of the extended surface elements may give a considerable reduction of the initial costs, since for the same furnace efficiency it is necessary to have only about one-half as many extended surface tubes as bare tubes. Unfortunately, refinery fuels high in solid content frequently prevent the wide use of the extended surface. In such cases the solids are deposited on the extended surface and make heat transfer and draft conditions difficult. Where the refinery fuel is gas, extended surface tubes may be used without the difficulties mentioned above.

The temperature of the combustion chamber (approximately 10 inches below that of radiant tubes) is usually from 650 to 850°C. (1202-1562°F.). The temperature of the flue gases in the outlet from the convection section is from 425 to 550°C. (797-1022°F.). The high temperature of the flue gases leaving the convection chamber is due to the high temperature of the charging stock entering the furnace. It should be remembered that the inlet temperature of the charging stock is usually close to 300-350°C. (572-662°F.) so that the minimum temperature of flue gases leaving the furnace should be about 425-500°C. (897-932°F.).

Coke formation in tubes is closely related to heat transfer. In the advanced stages of cracking, when conversion is close to the allowable crack per pass, coke formation may take place in the body of the cracking

stock. More frequently it occurs in the film or skin on the inner surface of the tubes. As a matter of fact, the temperature in the oil film is somewhat higher than in the body of the cracking stock. Thus the extent of cracking corresponding to the beginning of coke formation may be attained in the film much more easily than in the body. According to the computation of Nelson,²⁴ the film temperature in the radiation tubes, which receive radiation at the rate of about 5500 B.t.u. per sq. inch of outside surface per hour, would be 47.5°F. higher than the inner temperature of the fluid. This difference corresponds to the clean surface of the tube. If a coke deposit $\frac{1}{8}$ inch thick is produced, the film temperature would be 145.5°F. higher than the inner temperature. Thus the deposition of coke creates conditions favorable to local overheating and enormously increases coke formation in the highly overheated film. It is evident that the temperature in the film directly depends upon the rate of heat transfer. Excessive heat transfer rates should be avoided in the tubes where conversion is high, and close to the beginning of coke formation.

The coke deposited in the tubes is periodically removed by the cutters driven by high-speed turbines. Garrard¹⁵ described a new steam-air decoking method. With this method the coke is loosened by a combination of furnace heating, steam flow through the tubes and injection of small amounts of compressed air. After four to six hours, the volume of air is increased, and finally pure air is pumped for burning out the last portions of coke. The greater part of the coke is removed in the form of solid coke particles ranging in size from dust to pea size. This method eliminates the removal of return bends before cleaning. The costs are claimed to be from 35 to 100 per cent of costs by the mechanical methods.

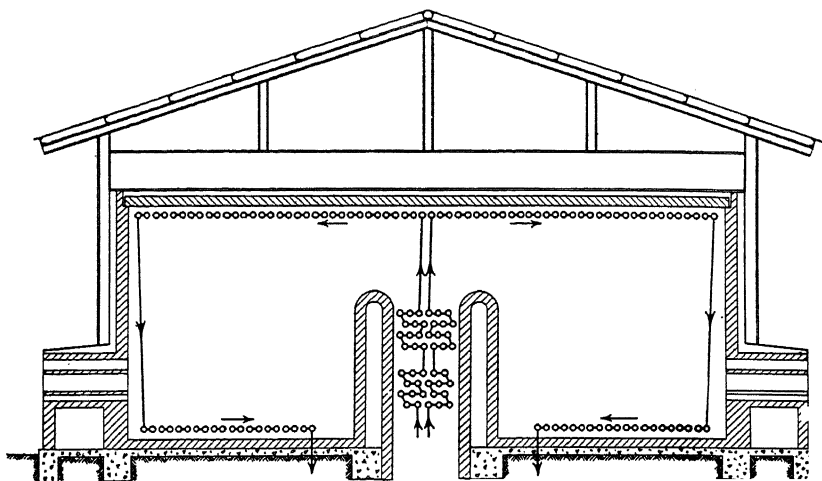
Tube Heaters

The radiant tubes are installed on the roof, floor and walls of the conventional box-type furnace. In the DeFlores cylindrical heaters they are located on the wall and in the Equiflux heaters in the middle of the combustion chambers. The wall and particularly the roof radiant tubes are frequently arranged in two rows. The ratio between the heat input to the tubes of the first and second row is about 100:35. As a general rule, more than two rows are seldom used in practice due to a very small heat input to the third row, which amounts to only 10-15 per cent of that obtained by the first row.

The convection tubes are usually installed in a single section located between the combustion chamber and the stack.

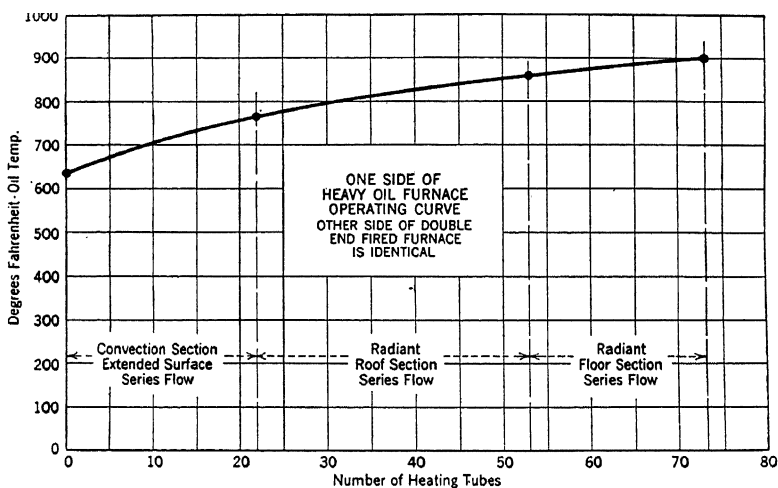
Box-type Furnaces

The arrangement of the radiant and convection sections, as well as the location of soaking tubes, in box-type furnaces (Foster Wheeler Corporation) is illustrated by Figures 17 and 19. The temperature of the charging stock in the furnaces is shown in Figures 18 and 20 respectively.



Courtesy Foster Wheeler Corp.

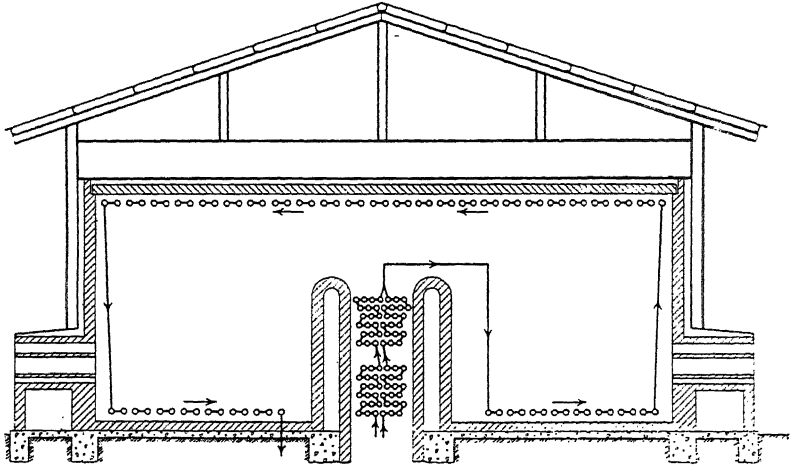
FIGURE 17.—Foster Wheeler Heavy-oil Cracking Furnace.



Courtesy Foster Wheeler Corp.

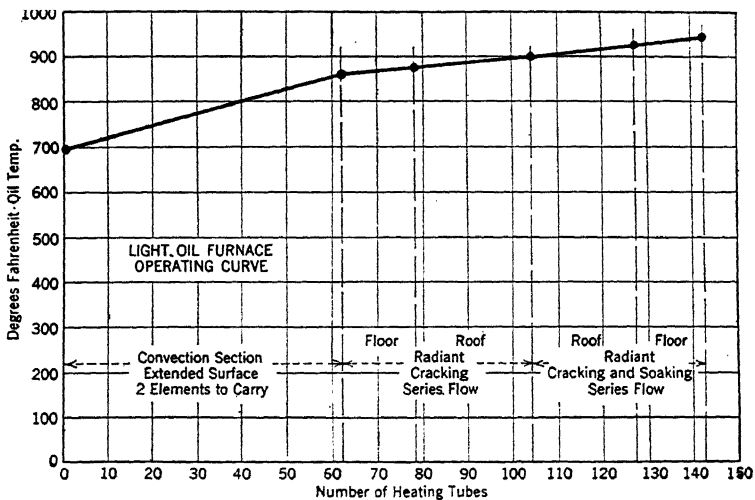
FIGURE 18.

These two furnaces are used for the selective cracking of heavy and light feed from topped Iraq crude. The heavy oil cracking furnace (Figures 17 and 18) is divided into two identical heaters with a common convection section. The charge is divided into two equal parallel streams which pass through the convection section, through the radiant roof tubes and then through the radiant floor tubes. A part of the radiant



Courtesy Foster Wheeler Corp.

FIGURE 19.—Foster Wheeler Light-oil Cracking Furnace.

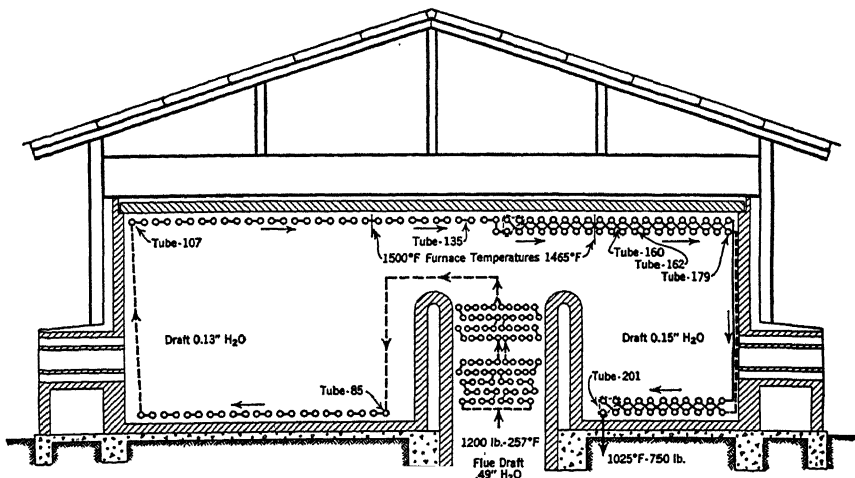


Courtesy Foster Wheeler Corp.

FIGURE 20.

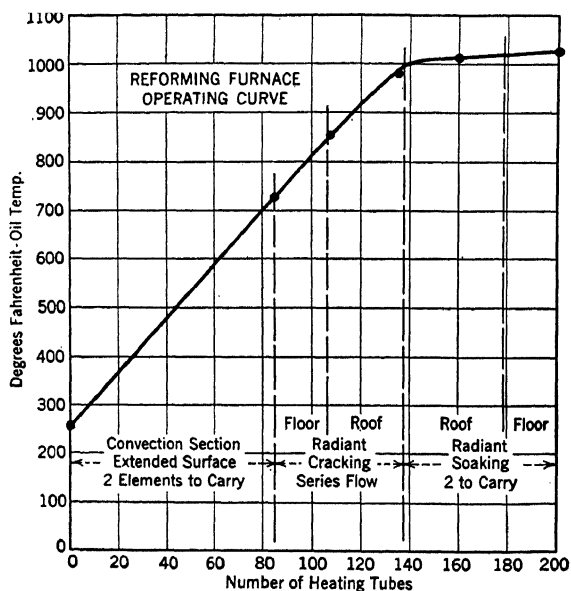
floor tubes is a soaking section of the heater. In this furnace the soaking section is not separated from the preheating section.

The design of the light oil cracking furnace (Figures 19 and 20) is substantially different. This furnace has a separate radiant soaking section which is fired independently of the heating section. The charge is pumped through the convection section in two parallel equal streams.



Courtesy Foster Wheeler Corp.

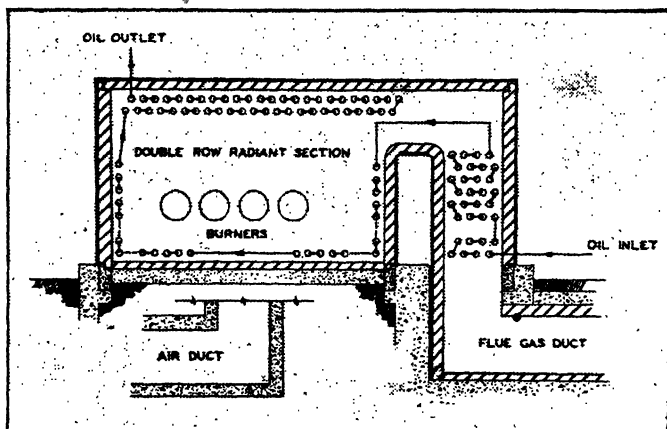
FIGURE 21.—Foster Wheeler Reforming Furnace.



Courtesy Foster Wheeler Corp.

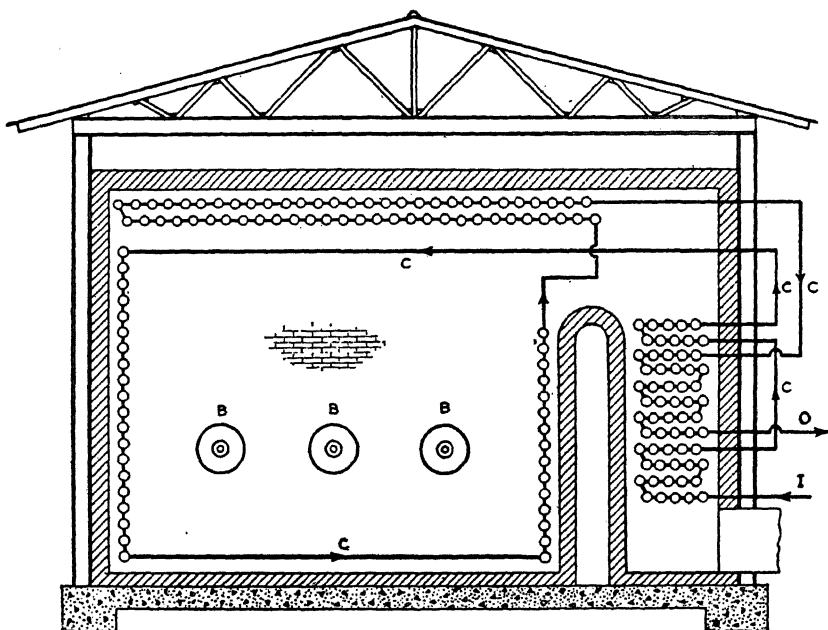
FIGURE 22.

These are combined at the outlet from the convection section and flow through the floor and roof tubes of the righthand radiant section, then through the roof and floor tubes of the lefthand radiant section. The



Courtesy "Oil and Gas Journal"

FIGURE 23.—Single Radiant Section Furnace; Soaking Tubes in Radiant Section.

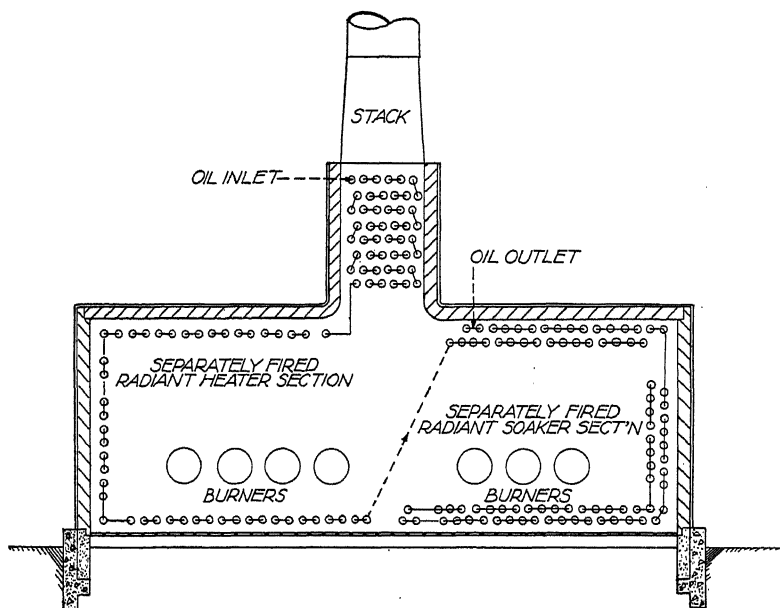


Courtesy "National Petroleum News"

FIGURE 24.—Single Radiant Section Furnace; Soaking Tubes in Convection Section.

lefthand radiant is the soaking section. Due to complete separation of heating and soaking, this type of cracking furnace has maximum flexibility.

The Foster Wheeler reforming furnace (Figures 21 and 22) is similarly designed. The charge passes the convection section in two equal parallel streams, then passes the lefthand radiant section in one combined stream, and finally the righthand radiant section in two parallel streams again. The righthand radiant section in this furnace is the soaking section, where the temperature of the charge rises at a very low rate from 1000°F. to 1025°F. as will be seen in Figure 22.



Courtesy "Oil and Gas Journal"

FIGURE 25.—Central Overhead Convection Section Furnace with Two Radiant Sections.

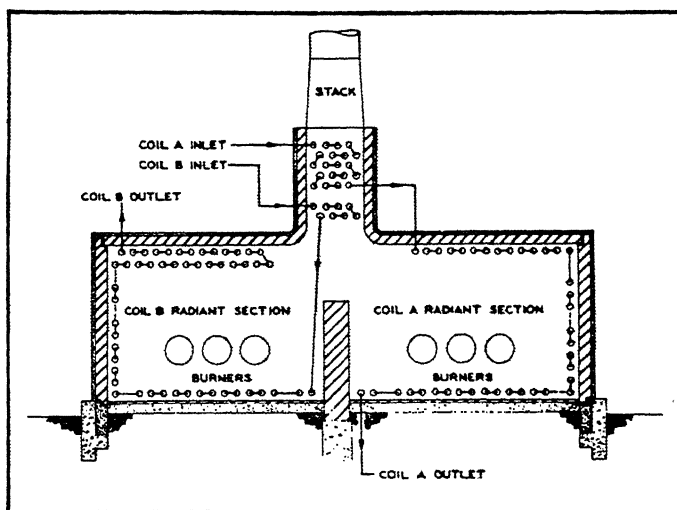
In other box-type cracking furnaces the soaking sections are located as shielded rows of tubes.²⁸ In the single radiation furnace (Figure 23) the charge is heated in the convection section and then in the wall and roof tubes of the radiant section. The roof tubes of the second row are soaking tubes. They are shielded by the tubes of the first row and heated to a more moderate extent to keep the cracking temperature approximately constant.

A soaking section located in the convection section is represented in Figure 24. The charging stock enters the tubes in the lower part of the convection section, and moves upward to the upper part of the section without reaching the middle part. From the upper part of the convection section the charge passes through the wall and roof tubes of the radiant section and finally enters the middle part of the convection

section. The tubes in this part of the convection section are soaking tubes shielded by the upper rows of the convection tubes.

In the aforementioned schemes the convection section is separated from the radiant sections by a bridge wall. The convection sections may be built above the radiant section. Figure 25 shows a furnace with two separate radiant sections, heating and soaking, and with the convection section located between the radiant sections and the stack. This construction eliminates a comparatively expensive bridge wall.

As has been mentioned above (p. 137), combination units or units for selective cracking may have many separate cracking tube heaters, as many separate cracking operations take place in the unit. However,



Courtesy "Oil and Gas Journal"

FIGURE 25a.—Double Radiant Section Furnace with Overhead Convection Section.

two or more separate cracking coils are frequently located in the same furnace, as shown, for instance, in Figure 25a. In this scheme two different cracking operations are performed in two separate coils. A part of the convection section and the first radiant section are used for the first coil and operation, and another part of the convection section and the second radiant section are used for the second cracking operation.

The Alcorn radiant furnaces (Nash and Alcorn²⁶) may also be classified as box-type tube heaters (Figure 26). Here the process of combustion takes place in special silicon carbide canals, R, the walls of which readily radiate heat. Here the tubes of radiant sections are completely protected from the action of the flame, allowing the silicon carbide furnaces to be made comparatively low. The convection section is located above the radiant section.

It should be mentioned that short silicon carbide canals or muffles are sometimes used in other furnaces.

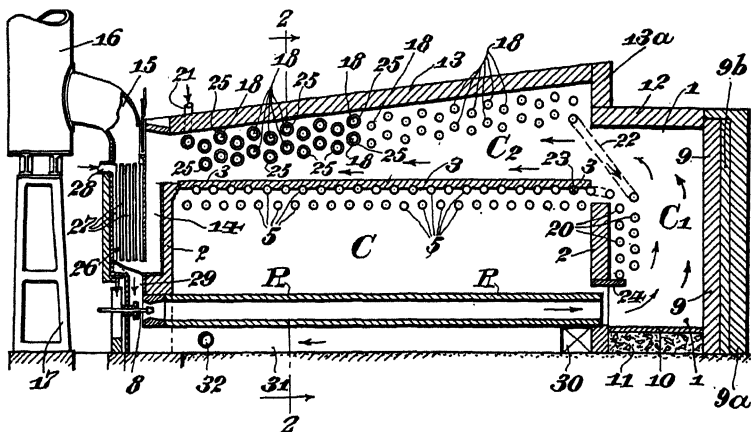


FIGURE 26.—Alcorn Combustion Furnace.

DeFlorez and Equiflux Furnaces

In contradistinction to the box-type furnace, the DeFlorez furnace is cylindrical and consists of a vertical cylindrical shell with tubes arranged in a circle against the inner wall.

The DeFlorez heaters are of the downshot and upshot types. Figure 27 represents an upshot furnace with the burners at the base of the combustion chamber, with an economizer bank and air preheater superimposed over the combustion chamber. Such a design involves no difficult draft problems, as the height of the furnace itself affords much of the draft required. A short stack of 25 to 50 feet is built above the air preheater to overcome the friction developed by the movement of the flue gases up through the economizer and air preheater.

In the DeFlorez heater the radiant heat zone is designed so that the charging stock will absorb from 75 to 100 per cent of the total heat input in this zone, depending on whether or not an economizer bank is employed.

The vertical tubes are hung from the upper tube sheet, which is supported by columns which also support the steel shell with its refractory and insulating lining. The vertical tubes are usually staggered, being placed in two concentric circles. These are arranged on wide centers with plenty of clearance between the tubes in the inner row nearest the flame so that these tubes do not shield the outer tubes.

The diameter of the combustion furnace is fixed by the heating surface requirement, particularly in the larger furnace sizes where maxi-

mum tube length of 34-45 feet is required. These vertical heaters are being used extensively in conjunction with high-temperature cracking units where the charge is raised to a temperature approximating 593°C. (1100°F.). For these high temperatures ordinary steel tubes are used

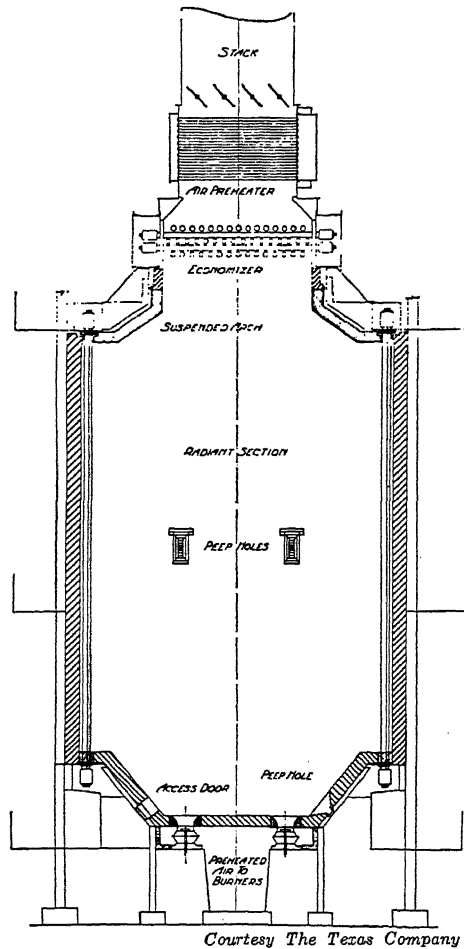


FIGURE 27.—Upshot DeFlorez Furnace.

throughout. It is claimed that runs of more than 1500 hours have been made, and that tubes have not been cleaned for six months where DeFlorez heaters have served vapor-phase cracking plants. The air preheater in an all-radiant furnace without any economizer section is constructed of a special heat-resisting alloy metal, while in a furnace where the air preheater is shielded from the flame by the economizer section below, ordinary carbon steel tubes may be used.

The smaller DeFlorenz heaters built to-day contain a vertical radiant section having approximately 670 square feet of tube surface. The shell of the combustion chamber measures approximately 12 feet in diameter inside the brickwork. The larger upshot furnaces contain about 5,500 square feet of tube surface, the combustion chamber being 25 to 27 feet in diameter inside the brickwork.

Leslie²¹ described a new DeFlorenz furnace of the downshot type (Figure 28). The furnace is equipped with a brick cone which is claimed

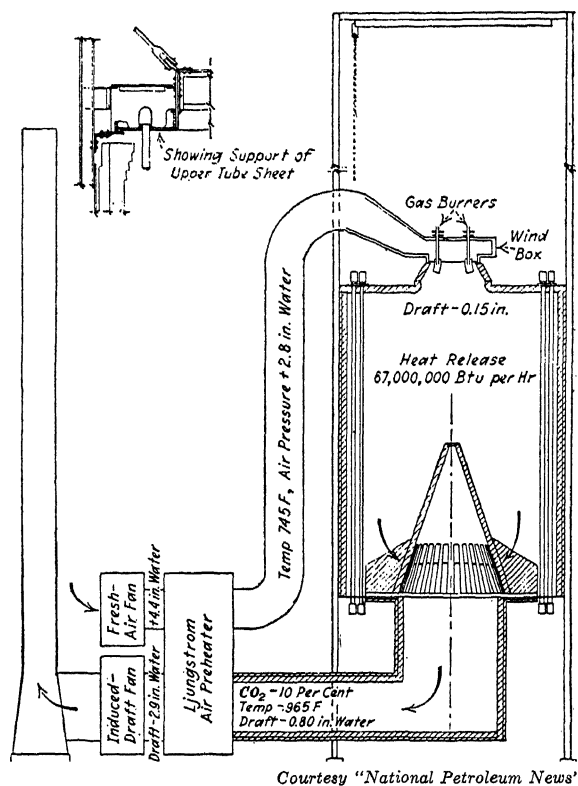


FIGURE 28.—Downshot DeFlorenz Furnace.

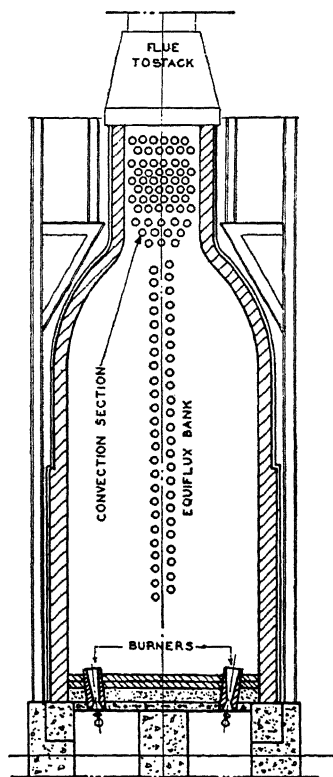
to improve the heat distribution. The designed capacity of the furnace is 20,000 gallons per hour. The internal diameter of the furnace is 28 feet 9 inches and the height 45 feet, not including the foundation and superstructure. The furnace contains 152 tubes, 4 inches outside diameter, 5 inches inside diameter, arranged in two concentric circles. The approximate heat transfer is 7000 B.t.u. per square foot of outside surface per hour.

In comparison with box-type heaters, the location of tubes in the

DeFlorez heaters is not convenient for handling and requires a comparatively expensive superstructure.

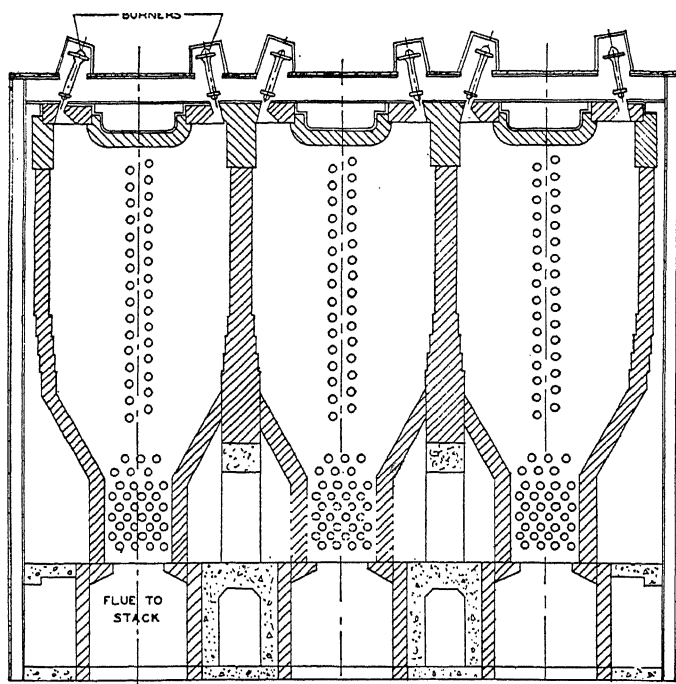
In box-type furnaces, as well as in cylindrical DeFlorez furnaces, described above, the radiant tubes are directly irradiated only on the side exposed to the flame. The other side is irradiated by the reradiation from the wall or roof. A direct radiation of tubes from both sides can be obtained by the arrangement of tubes between two sources of radiation. The Equiflux furnaces, using irradiation from both sides, are claimed to be more effective and to give higher heat transfer rates, amounting to 15,000-20,000 B.t.u. per square inch of outside surface per hour.²² Figure 29 represents the scheme of a single-cell furnace Equiflux heater with the burners at the base of the furnace. The convection chamber is located above the combustion chamber. Figure 30 shows the scheme of a 3-cell Equiflux heater with separating walls of non-suspended refractories. The burners are at the top of the combustion chamber and the convection sections are at the base of the furnaces. Each cell has a separate convection section. A centralized convection section for several cells may also be used. The different cells in multi-cell Equiflux heaters may be used in various ways, for instance, for cracking parallel streams of charging stock; for heating the charging stock to cracking temperature in one cell and for controlled soaking in another cell; and for selective cracking of various distillates, using each cell for each distillate.

A direct heating of cracking and soaking tubes by radiation or by hot combustion gases is used in all operating cracking units. As has been stated above, heat transfer by radiation or convection can be controlled very thoroughly. Therefore heating by fluid heating media, such as molten salts or metals, is not employed in commercial units. There are, however, a few patents covering the use of molten materials transferring heat to the cracking stocks. The heat transfer may be either direct, when the cracking stock is in direct contact with the molten material, or indirect, when the cracking stock is pumped through tubes located in the molten material. The latter method of heat transfer is used in some small experimental cracking units.



Courtesy "National Petroleum News"

FIGURE 29.—Single-cell Equiflux Furnace.



Courtesy "National Petroleum News"

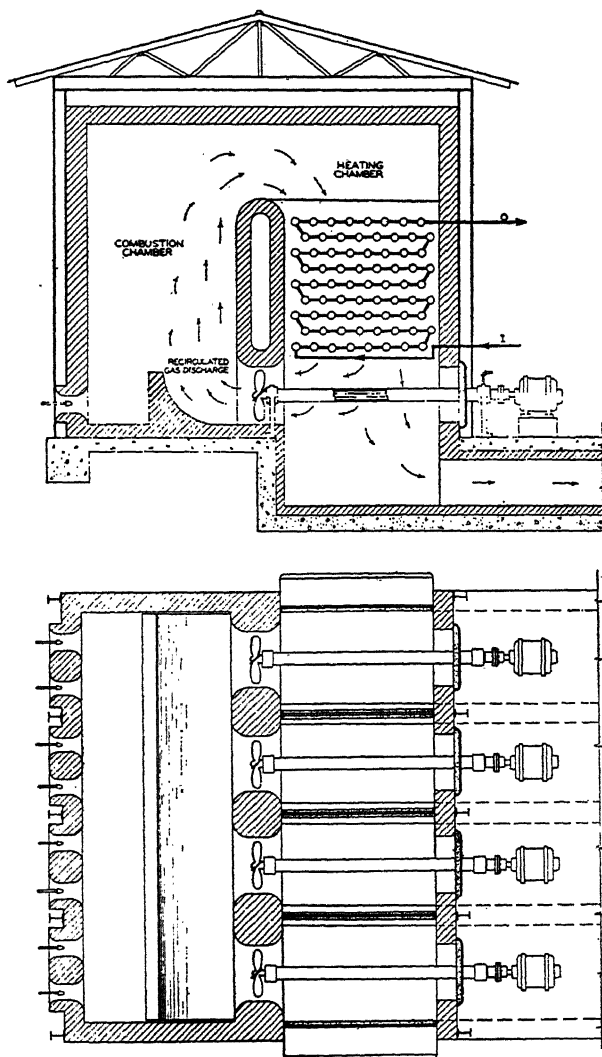
FIGURE 30.—Three-cell Equiflux Furnace.

Recirculation of Flue Gases and Air Preheating

The recirculation of flue gases to the combustion chambers was extensively used a few years ago. A part of the flue gases is recirculated to the furnace by a fan with the result that a part of the heat which they contain is recovered, and the temperature in the furnace decreases. Thus the temperature in the furnace and the rate of radiant absorption are lowered, and are controlled by the extent of recirculation. A recirculation ratio (quantity of recirculated flue gases to that of fresh gases of combustion) varies from 1:1 to 4:1. No radiant tubes may be employed in the recirculating furnaces with a high recirculation ratio, and in such furnaces all heat input is performed in the convection section. Figure 31 represents a conventional recirculating furnace without radiant tubes—a type in general use ten years ago and still used in many refineries.

The high operating and maintenance costs of the recirculation of flue gases are a serious drawback to this method. The recirculation of flue gases has been introduced in refinery practice by Bell and is covered by his patents.⁴ It is not employed in modern cracking furnaces, in which the absorption of radiant heat is controlled by proper development

of the surface absorbing the radiation. In contrast to earlier furnaces, a very small excess of air is used in modern radiant furnaces, not exceeding 20-25 per cent. As has been mentioned above, a large percentage of



Courtesy "National Petroleum News"

FIGURE 31.—Flue Gas Recirculation Furnace.

excess air, as well as recycling of flue gases, was employed in earlier furnaces to control the temperature of the combustion chamber and heat transfer rates.

The preheating of air for combustion is largely used in modern furnaces for cracking. The fresh air is passed through the tubes of the preheater or economizer, where it is preheated by the flue gases before it enters the burners. The air is usually preheated to 250-300°C. (482-572°F.). The preheating of air reduces the consumption of fuel and increases the flame temperature, which results in increasing radiation.

The pressure drop in the coil depends upon many factors, the most important being the throughput and diameter of the tubes. The usual difference in the pressures between the charging hot pump and outlet of the coil is from 200 to 600 pounds per square inch gauge.

The following factors contributed to the latest development in the design of tube heaters and other parts of cracking equipment:

1. The use of higher temperatures in cracking or in thermal conversion of gases.
2. Combination of cracking with straight-run distillation.
3. Selective cracking in different tube heaters or different sections of a single heater.
4. Very large capacities of many modern combination units, up to 30,000 barrels per day and more.
5. A better utilization of radiant heat.
6. Higher average heat transfer rates particularly for radiant heat.
7. An extensive use of tube soaking sections, instead of reaction chambers with controlled heat transfer rates in these sections.

Other Parts of Cracking Equipment

The synthetic crude passes from the cracking coil either directly to the separating parts of the cracking unit or to the reaction chamber, when the latter is used in the process.

The reaction chamber usually is properly insulated and not heated at all. The heat imparted to the charging stock in the cracking coil is sufficient to effect further cracking in the reaction chamber. The temperature of the synthetic crude being cracked decreases appreciably in the reaction chamber in the absence of additional heating, due partially to losses by radiation but mainly to the heat absorption resulting from the cracking and the processes of evaporation. The difference in the temperature in the inlet and outlet of Cross reaction chambers is about 30°C. (54°F.) or slightly more.

The size of the reaction chambers varies depending on the process. In high-pressure cracking units, such as Cross units, the chambers are comparatively small; for instance, the reaction chamber of a unit having a capacity of 3000 bbls. of fresh stock per day is 6 feet I.D. x 40 feet. In these reaction chambers only cracking takes place to a required extent without separation of distillates from the residuum.

In cracking units operating under moderate pressures, such as Dubbs units, the size of the reaction chambers is much larger; for instance, the reaction chamber of a unit having a daily capacity of 2000 bbls. is 10

feet I.D. x 40 feet. The Dubbs reaction chamber provides not only the required extent of cracking, but also the separation of distillates from the residuum.

As has been mentioned above, the separation of distillates from the residuum in high-pressure units is effected in special evaporators, operated under low pressures, from 30 to 75 pounds per sq. inch gauge, the pressure release valve being located between the outlet of the soaking tubes (or of the reaction chamber) and the evaporator. Here an advanced evaporation of the lighter parts of the synthetic crude takes place. The distillates formed in the evaporator pass through the top of the latter, while the heavier parts remain in the bottom, producing a cracked residuum which is continuously withdrawn from the evaporator.

Due to the fact that the temperature of the synthetic crude in the evaporator may be comparatively high, up to 450-500°C. (842-932°F.) or even higher, the evaporation may become very intense. This may result in a residuum which is too heavy and asphaltic to be marketed. There is also a possibility of coke being formed in the evaporator because of the progressive cracking at such high temperatures. Therefore, cooling down to discontinue the cracking and to prevent excessive evaporation is effected by one of the following two methods.

In the first method, the evaporator is provided with a coil or heat exchanger, through which fresh stock is passed to reduce the temperature in the evaporator. In the second, more efficient quenching method, fresh cold stock is pumped into the stream of synthetic crude before it is released into the evaporator. The quenching stock may be preheated to a certain extent before quenching. On the other hand, other products, such as cooled residuum, water, etc., may replace the charging stock in the quenching operation.

The quenching may also be carried out in the evaporator or in a special chamber (arrester), as in the Gyro units. The extent of quenching depends on the temperature of cracking. The charging stock, cracked at the high temperature of the vapor-phase process, requires more quenching than stock cracked at more moderate temperatures.

The quenching method has been proposed and patented by Weaver³² for vapor-phase cracking and by Donnelly¹¹ for pressure-cracking.

The temperature in the evaporators is kept from 350-425°C. (662-797°F.). The level of the residuum in the evaporator predetermines the time during which the residuum remains in the evaporator. The higher the temperature in the evaporator, the shorter should be the time. Table 114 gives the allowable time during which the residuum may remain in the evaporator without appreciable coke formation, *versus* the temperature in the evaporator.

The vapors and gases from the evaporator in high-pressure units and from the reaction chambers in moderate-pressure units enter the fractionating or bubble tower, which produces gasoline or naphtha of the required end point, and recycle stock for repeated cracking. A few years

Table 114. Temperature and Allowable Time During Which the Residuum Remains in Evaporator.

Temperature		Time (hrs.)
°C.	°F.	
380	716	4
390	734	2
400	752	1
410	770	0.5
420	788	0.25

ago, the production of end point gasoline in cracking units was not very important, due to a wide use of the sulphuric acid treatment. This method of treatment requires redistillation of the treated distillate to remove high-boiling products formed in the treatment (page 355). As a result, pressure distillates with comparatively high boiling points were frequently produced in cracking units. At the present time, cracking units produce cracked gasolines or naphthas of specified end point to be used directly as commercial gasolines after sweetening and inhibiting.

The design of the bubble towers in cracking units should also provide a side stream of furnace oil which is frequently withdrawn from cracking units (pages 161 and 378).

The pressure in the bubble tower should be at least 30 pounds per square inch gauge. An elevated pressure in the bubble tower has many important advantages. In addition to the smaller size of the bubble tower operating under pressure, the elevated pressure increases the temperature of the recycle stock. The condensation of vapors from the bubble tower under the same elevated pressure produces gasolines containing most of the butanes and butenes formed in cracking. As a result, no absorbers, expensive in first cost and operation, need be used for complete extraction of hydrocarbons usable in motor fuel. Finally, an elevated pressure in the bubble tower is essential for the operation of charging hot pumps. As a matter of fact, the temperature of the recycle stock, which is obtained in the bottom of the tower, is high—about 300°C. (572°F.) or more—and the performance of the hot-oil pump used for recirculating this stock and fresh feed would be greatly impaired by vapor lock if the operation were carried out at low pressure, because of the evaporation which would occur at the high temperature.

The temperature conditions in the bubble towers of cracking units depend on the pressure. If the pressure is about 30 lbs., temperatures of about 185°C. (365°F.) in the top and of about 315-340°C. (644-599°F.) in the bottom of the bubble tower are maintained. Higher temperatures are employed at higher pressures.

The residuum from the evaporator (or from the reaction chamber in Dubbs and Holmes-Manley units) passes into a flash chamber, which is maintained under atmospheric pressure. The separation of the residuum from distillates in the evaporator or reaction chamber is fairly rough, and, as a result, the residuum contains a large proportion of light distillates, up to 30 per cent or more (page 390). These distillates are

flashed in the flash chamber, where they are separated into distillates and a final residuum or cracking tar. The flashing chamber may be operated under subatmospheric pressure also.

Other parts of the cracking equipment, such as coolers, stabilizers, etc., are of conventional design and are beyond the scope of this book.

The temperature of the charging stock entering the furnace is a very important factor. The higher this is, the lower is the heat input in the furnace. Thus the size and the first cost of the furnace depend on the temperature of the charging stock. In modern cracking units the temperature of the entering charging stock is very high, up to 350°C. (662°F.), as has been stated above. A further increase in this temperature involves some difficulties. On the other hand, a higher temperature of the entering charge would considerably increase the temperature of the flue gases leaving the furnace, and offset the advantages of further preheating. Thus in modern cracking units the large waste heat of cracking products is used for other processes not connected directly with cracking, such as distillation, stabilization, etc. (Chave⁷). From this standpoint, the combination of cracking with straight-run distillation is particularly advantageous. The heat exchange between the cracked products with high content of heat and the crude oil may take place either directly in fractionating columns or indirectly in heat exchangers. Special high-pressure-temperature heat exchangers are used for the preheating charging stocks pumped under high pressure (Leach¹⁹).

In some old cracking units the temperature of the charging stock entering the furnace is comparatively low, about 200°C. (392°F.). For such cracking units preheating the charging stock gives a saving in the fuel consumption and an increase in the throughput. The extent to which a higher heat recovery can affect the throughput of a cracking unit is demonstrated by the two following examples: (1) In a Cross unit having a throughput of 3,280 barrels when running on a feed stock preheated to 207°C. (405°F.), the throughput was increased to 4,300 barrels on preheating the stock to 308°C. (587°F.). (2) In another unit when the feed temperature was raised from 222°C. (432°F.) to 243°C. (470°F.) the throughput was increased from 3,800 barrels to 4,800 barrels.

As has been mentioned above, the temperature of flue gases leaving the convection section of cracking units is high, about 450°C. (842°F.). The high heat content of flue gases is only partially utilized for preheating air, and a great part of the heat content remains in the flue gases leaving the economizer. This heat not usable for cracking can be utilized for other processes not connected directly with cracking. In the combination units this waste heat may be used for straight-run distillation. In some Tube and Tank furnaces a part of the large convection chamber is used as a reboiler section and a steam superheater. In this way the utilization of the heat content of flue gases is very complete, and the temperature of the flue gases leaving the furnace decreases to 315°C. (600°F.) or even lower.

The number and design of burners in cracking furnaces are of primary importance. The number of burners must be sufficient to ensure uniform distribution of heat in the furnace. Thus the amount of fuel consumed predetermines the number of burners. The average consumption of fuel per burner per hour is from one to $1\frac{1}{2}$ barrels. The mixing of air and fuel in burners must be very efficient to effect fast and complete combustion as well as a short flame. Short flames producing a higher radiation are preferable in modern radiation furnaces. Combination burners for liquid fuel and gas are commonly used in cracking furnaces. Rapid change from one fuel to the other must be secured.

The mechanical construction of cracking furnaces, as well as the description of various controllers and recorders widely used in cracking units, are beyond the scope of the present volume.

Tubes for Cracking Coils; Corrosion

Low-carbon steel is extensively used for the tubes of cracking furnaces, unless the temperature-pressure conditions are too severe, or highly corrosive charging stocks are employed.

It is well known that steel at temperatures exceeding 400°C . (752°F .) becomes semi-plastic and begins to creep non-elastically, after being subjected to high pressures for a long time. As a result, steels with low creep strength have a short period of service under high temperature-pressure conditions of cracking. The creep strength of a steel is a pressure that will not cause an elongation of more than 1 per cent at a given temperature and for a certain period of time, for instance, 10,000 or 100,000 hours.

Addition of a small percentage of chromium or molybdenum to low-carbon steels markedly improves their creep strength. Plain-chromium steels have embrittling properties after heating in service. Molybdenum steels do not have these tendencies; moreover, a small proportion of molybdenum, 0.5 per cent, in chromium steels overcomes their embrittling tendencies. Thus molybdenum and molybdenum-chromium steels are widely used for cracking. The creep strength of various steels is given in Table 115, according to data of Nelson.²⁴

If non-corrosive stocks are processed, plain carbon steel may safely be used for temperatures of about 500°C . (932°F .), depending on the pressure. Molybdenum steel with 0.5 per cent molybdenum, or molybdenum-chromium steel with 0.5 per cent molybdenum and 2 per cent chromium, may be used up to $550\text{--}600^{\circ}\text{C}$. ($1022\text{--}1122^{\circ}\text{F}$.).

The oxidation of tubes by combustion gases is of secondary importance, at least at the comparatively moderate temperatures of pressure and vapor-phase cracking. The oxidation and scaling of tubes is greatly reduced by addition of chromium or silicon.

Another important factor in the use of alloyed steels in cracking is the corrosive properties of charging stocks. The corrosiveness of crudes and distillates in cracking may be caused either by certain inorganic

Table 115. Creep Strength and Other Properties of Various Steels.*

Material	Carbon	Chromium	Nickel	Molybdenum	Yield point	Tensile	Elongation	Reduction of area	Brinell hardness	Pounds allowable stress limit for 1% creep in 100,000 hours		
										800°F.	900°F.	1,000°F. 1,200°F.
Carbon steel	0.30				45,000	74,000	26	35	137	9,350	4,600	2,200 400
Carbon-molybdenum	0.28			0.50	55,000	85,000	20	40	175	15,500	9,350	3,600 450
Nickel-chromium-molybdenum	0.30	0.80	2.00	0.40	75,000	105,000	21	40	197	17,875	10,675	4,725 1,000
Chromium-molybdenum	0.28	2.00		0.50	60,000	85,000	22	40	202	16,850	16,025	7,100 1,350
Chromium-molybdenum	0.22	5.00		0.50	75,000	105,000	20	45	195	21,000	14,700	6,100 1,100
Chromium-molybdenum	0.12	9.00		1.50	50,000	80,000	25	50	190		24,750	5,800 1,600
18-8	0.15	18.00	8.00			80,000	40	45		14,725	14,100	13,000 4,550

* Basic Type Steels used for Oil Refinery Service.

chlorides or by organic sulphur compounds. Such substances as magnesium and calcium chlorides are hydrolyzed in the presence of steam at high temperatures, with formation of highly corrosive hydrogen chloride. It should be mentioned that the content of inorganic salts in some crudes has appreciably increased during recent years owing to the increasing practice of acidizing wells. The de-emulsification of crudes and the separation of brine before cracking is still an important prerequisite to eliminate or at least to reduce corrosion.

The reactions involved in high-temperature corrosion by sulphur compounds are not completely clear. It is probable that the formation of corrosive elemental sulphur, mercaptans and particularly hydrogen sulphide from various sulphur compounds of charging stocks is a preliminary stage in the corrosion caused by charging stocks rich in sulphur.

Both factors in the corrosion, inorganic salts and sulphur compounds, may be of importance in the viscosity breaking process, while sulphur compounds are primarily responsible for corrosion by cracking distillates.

Molybdenum steels containing 0.5 per cent molybdenum are not resistant to corrosion. Addition of chromium effectively increases the corrosion resistance of steels. The corrosion resistance of chromium steels containing from 1 to 1.5 per cent chromium is approximately 2-3 times greater than that of plain carbon steel. For highly corrosive charging stocks and high temperature-pressure processes steels containing a large proportion of chromium are used, as for instance those containing from 4 to 6 per cent chromium and 0.5 per cent molybdenum. The corrosion resistance of this steel is 5-6 times that of plain carbon steel. This property of chromium and some other metals is due to the formation of carbides more stable than those formed by iron. The chromium carbide is dissolved in iron carbide or forms a separate carbide, when the iron carbide becomes saturated with the chromium compound.

Addition of other elements, such as silicon, aluminum, etc., may give further improvement in the high-temperature and corrosion-resistant properties of steels.

Stainless steels with high content of chromium and nickel, for instance 18-8 alloy (18 per cent chromium and 8 per cent nickel), very resistant to corrosion and of very high creep strength, are seldom used in refinery practice due to a high cost of these special steels. They can be frequently replaced by steels containing 4-6 per cent chromium, 0.5 per cent molybdenum and 1-2 per cent silicon.

It is understood that tubes made of special steels may be used only for more severe temperature conditions, for instance, in radiant and soaking sections. The tubes of plain carbon steel can be used in other sections, particularly for non-corrosive charging stocks.

Other parts of the cracking equipment, such as reaction chambers, bubble towers, etc., may be protected by lining the inner surface of the apparatus with corrosion resisting alloys.

According to Shaler,²⁹ the results of chromium plating in the refinery

practice are very satisfactory. A special low-carbon chromium steel with 2 to 13 per cent chromium is employed for linings. The thin 15-gauge sheets of the chromium steel are plug-welded to the shell through 9/16-inch diameter holes on 4-inch centers. The lining costs run between \$5 and \$10 per square foot.

Another, but less popular means of protecting vessels from corrosion is the metal-spray method. Johnson and Dewey¹⁷ reported on the satisfactory results obtained for Dubbs reaction chambers metallized with aluminum. The reaction chambers protected by this method have suffered no measurable corrosion for 4½ years, compared with a previous average annual loss of 0.036 inch. The thickness of coating ranges between 0.0015 and 0.0020 inch. The cost of metallizing is 80 cents per square foot.

In addition to metallic linings, non-metallic linings can also be used. Dixon¹⁰ described the concrete lining or "gunite" which is applied with a cement gun. The gunite material consists of 1 part by volume of Portland cement and 2½ parts of fine sand. The thickness of the gunite lining varies from 1 to 1½ inches. Gunite is recommended particularly for the vapor space of vertical soaking chambers wherein the temperatures are from 850 to 900°F. and the pressures from 350 to 400 pounds per square inch. The service life of the gunite lining is about one year, and the cost from \$0.86 to \$1.11 per square foot.

On the other hand, an appreciable decrease in corrosion is produced by the use of lime. Dry hydrated lime of about 200 mesh is mixed with a portion of the charging stock in the proportion of 5 lbs. of lime to one gallon of stock, in a drum provided with a stirrer. The mixture is continually injected into the charging stock in the proportion from ¼ to 1 lb. per barrel of charge.

Hot Pumps

Due to a high pressure and a large extent of recycling, the pumps of cracking units consume a large amount of power. In most of the modern cracking units the high-pressure hot pump serves to handle the mixture of recycle stock and fresh feed preheated to a high temperature. The temperature of this mixture reaches 350°C. (662°F.), and the pressure exercised by the pump amounts to 500-1000 pounds and more, depending on the system. Pressures as high as 3000 pounds per square inch may be used in hydrogenation and thermal gas conversion units. A few years ago most of the hot pumps were simple or compound steam pumps, because of their simplicity, reliability and ease of operation. The steam consumption of these pumps, however, is very high. Thus a hot pump of 600 pounds working pressure, a steam pressure of 135 pounds and a daily capacity of about 6000 barrels of the hot mixture consumes at least 3 to 3½ tons of steam per hour.

The steam consumption is lowered considerably by using fly-wheel steam pumps, or centrifugal turbine drive pumps equipped with con-

densers. Electric motor-driven power pumps give about the same saving of power. Gas engine pumps are most economical in operation, due to the low rates for gas, particularly in oil field regions. On the other hand, the first cost is much higher for the pumps which are most economical in operation. Tables 116 and 117 give the data on the first cost and operation of hot pumps of various types.

Table 116. First Cost and Operation Cost of Hot Pumps.²

Capacity of pump 6,500 bbls. of the hot mixture per day; pressure 1,450 pounds; steam pressure 100 pounds; cost of water for condensation, 1.1 cents per 1,000 gallons; cost of power, 1 cent per kilowatt-hour; cost of steam 30 cents per 1,000 pounds.

Type of Pump	Exhaust	First Cost	Yearly Exploitation (300 days)
Simplex-duplex or twin single	10 lbs. back pressure	\$13,500	\$27,868
Compound duplex or twin single	atmospheric	16,400	25,848
Compound duplex or twin single	with condensation	17,000	16,056
Power pump motor-drive		16,000	11,376
Centrifugal motor-drive		13,500	19,152
Centrifugal turbine drive	atmospheric	13,500	22,968
Centrifugal turbine drive	with condensation	15,000	14,356
Fly-wheel cross compound	atmospheric	21,800	9,720
Fly-wheel cross compound	with condensation	22,800	7,848

The Burton Process and Similar Processes

A comprehensive study of patents on cracking processes has been made by McKnight.^{21a}

Historically the first patents relating to present-day pressure cracking were taken out by Dewar and Redwood (1889) and Shukhov and Gavrilov (1891). Neither of these, however, gained practical application. The first semi-commercial vapor-phase processes of Greenstreet, Rittman, Alexander and Hall, described by Leslie,²⁰ were unable to overcome the difficulties connected with excessive coke formation. The first pressure-cracking system of wide technical importance was the Burton process, in which the process is carried out in the usual cylindrical horizontal still at 4 to 5 atmospheres pressure. The vapors of the cracked gasoline formed pass through the dephlegmator together with vapors of the undecomposed product, the dephlegmator returning the heavier condensed parts to the still for further cracking. The feed stock also enters through the dephlegmator. The temperature of the liquid being cracked does not exceed 400-410°C. (752-770°F.). This accounts for the low velocity of the process. The preheating and the cracking were not separated at all at first. The sedimentation of coke in the heating zone caused overheated spots.

The further modifications of the Burton system consist in separating the heating process from the decomposition process proper, which is conducted in the still. In the Clark modification the heating process is carried out in a number of inclined tubes connected with the reaction still. The measurements of the still were 10 by 40 feet, and 45 tubes of 4 inches diameter were usually used. The working cycle was three days, in which about half a pound of coke per barrel was formed when working with

Table 117. First Cost and Operation Cost of Hot Pumps.¹⁴

Capacity 334 gallons per minute or 11,500 bbls. per day; pressure 1170 pounds; steam pressure 100 pounds; cost of steam 27 cents per 1,000 pounds; cost of power $\frac{1}{8}$ cent per kw-hour; cost of gas 15 cents per 1,000 cubic feet; gas 1,500 B.t.u. per cubic foot.

Pump Size Pump Unit	Direct Acting		Fly-wheel, No Condensation		Electric Motor-driven Power Pump	Fly-wheel Cross Compound Condensation	Gas-engine Power Pump
	Direct Duplex	Duplex Compound	Twin Engine	Cross Compound			
	36 x 8¼ x 24	30 & 46 x 8¼ x 24	22 & 22 x 5 x 24	28 & 42 x 5 x 24	5 x 24	24 & 52 x 5 x 24	17 x 24 x 5 x 24
Pump Speed	60	60	45½	45½	45½	45½	45½
	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.
Exhaust Steam Pressure	Atm. 228	Atm. 228	Atm. 228	Atm. 228	299 H.P.	26" vacuum 228	269 H.P.
Horse Power	hydr. 76 lb.	hydr. 53 lb.	hydr. 40 lb.	hydr. 33 lb.	0.746 k.w.	hydr. 19 lb. steam 4332	7.67 Cu. Ft. Gas 2064
Power per H.P. Hour	steam 17328	steam 12084	steam 9120	steam 7524	223 k.w.	lb. 145	Cu. Ft. 2064
Power per Hour	lb. 578	lb. 403	lb. 304	lb. 251	14,701	8,811	2,336
Boiler H.P. Required	\$35,262	24,589	18,554	15,304	15,900	18,400	28,000
Cost per 314 days	\$12,500	17,300	16,000	17,400			
First Cost							

gas oil. The capacity of the unit did not exceed 200 barrels per 24 hours, while the yield of gasoline was approximately 35 per cent.

The Flemming cracking process was very similar to the original Burton process. The heating as well as the cracking reaction is carried out in the still, which is in a vertical position. The condensate from the dephlegmator is not returned directly to the still, but is added to the fresh stock which enters the still. The fresh stock is introduced through the dephlegmator. The working cycle is approximately three days. The heating temperature is about 400°C . (752°F .) and the pressure 100 lbs. The yields of gasoline and coke are approximately the same as in the Burton-Clark process.

In the Isom process the heating is carried out in parallel vertical tubes which are 20 feet high and have a diameter of four inches. After leaving the heating tubes the liquid enters the reaction still in which decomposition takes place. The dimensions of the still are the same as those of the Burton-Clark unit.

The decomposed products, together with the lighter undecomposed parts, enter the tower from which the condensate is returned to the reaction chamber. From the reaction chamber the liquid is pumped hot into the heating tubes. The pressure does not exceed 8 atmospheres. Thus in the Isom process the liquid in the reaction still circulates continuously through the heating tubes. The charging stock enters through the upper part of the tower connected with the still as is shown in Figure 32 for the Jenkins still. No data are available on the further development of the Isom process which is used in the Sinclair refineries. The latest patents of Isom, Herthel, Pelzer and others¹⁶ relate to modern types of cracking using a continuous coil and clean recycling.

The Jenkins process is quite similar to the Burton-Clark process. In this process the propulsion of the liquid in the heating tubes is accelerated by a special propeller or fan. Figure 32 shows the layout of the Jenkins unit. The stock, which is moved by a pump, passes first through a reflux tower and thence into a still equipped at each end with a drum. These drums are connected by parallel heating pipes (more than 100), which are not shown in the drawing. The propeller is placed in the riser from the lower drum and is driven at 600 revolutions per minute. A complete circulation of the liquid is effected in 20 seconds, due to the propeller. The pressure in the still and in the dephlegmator amounts to 80 to 200 pounds and the oil temperature amounts to 400 - 420°C . (752 - 788°F .). A reduction valve is provided between the dephlegmator and the column. Only 25 pounds pressure is maintained in the column. The gasoline and gas oil vapors pass from the reaction still through the dephlegmator into the column. Part of the gas oil condenses in the dephlegmator and flows back into the still.

The separation of gasoline from light gas oil is effected in the column, the light gas oil passing through the reboiler, and from it through the

condenser into the reservoir. The residue in the reaction still passes by way of the reduction valve into the expansion drum (5), where the pressure is lowered to atmospheric. Gas oil vapors liberated in this operation pass through the reboiler, in which they preheat the light gas oil in the column. From the reboiler, gas oil vapors which have been separated in the expansion drum pass through the condenser and thence into the reservoir. Thus in the Jenkins unit gas oil is produced in two parts of the equipment. These gas oils are taken out of the system and are further used by mixing with fresh feed stock. The oil obtained in

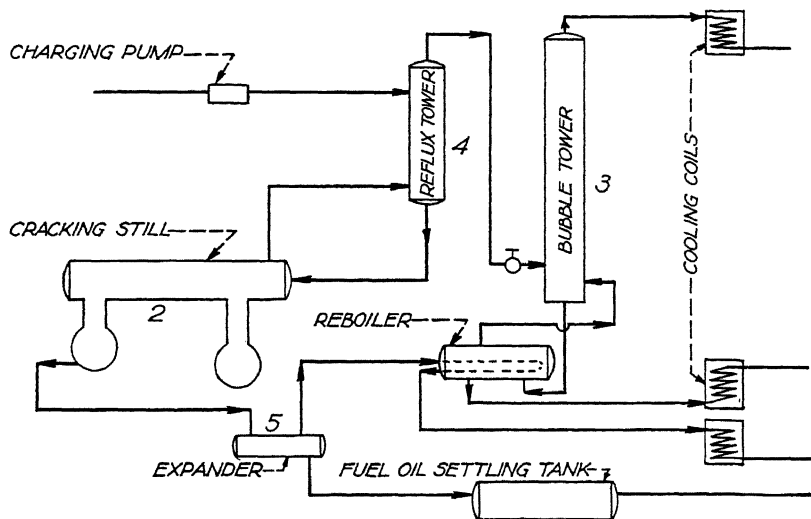


FIGURE 32.—Jenkins Cracking Process.

the expander is of comparatively high specific gravity, 0.825 to 0.850, and is characterized by the heavy fractions which it contains; while the gas oil from the column has a low specific gravity, 0.765 to 0.800, and is composed mainly of kerosene fractions. The final residue is obtained in the expander (5). The majority of the latest Jenkins cracking units have a daily charge capacity of 2000 barrels.

A feature of the Jenkins process is the use of lime which is admixed with the stock in quantities up to one-half to two pounds per barrel of charge. This not only effects a decrease in corrosion of the apparatus, which is the chief purpose for which it is used, but it also prevents precipitation of coke particles in the residue and so permits a long stream period [Jenkins, U.S.P. 2,167,211 (1939)]. Gas oils, fuel oils and heavy crudes can be cracked in Jenkins units.

The period under stream is long; it may extend through as much as two or three weeks. The performance of the Jenkins unit on Russian

stock of 0.875 specific gravity (together with recycling stock) is shown in Table 118.

Table 118. Yield of Cracked Products in the Jenkins Unit Run with Russian Stock.

Gasoline, 200°C. end-point	20% by vol.
Gas oil	65
Residue	13
Gas, losses and coke	2

The residue has a specific gravity of about 1.0 (10° A.P.I.), and less than half a pound of lime per barrel of stock is required. The working cycle is 30 days.

The Jenkins process is still used in a few European and Japanese refineries.

Principal Features of Old and New Cracking Processes

Three common features of the aforementioned processes are: (1) Heating of the charge in parallel tubes and in comparatively large reaction chambers. (2) The use of low or moderate temperatures, not exceeding 420°C. (788°F.). (3) Circulation of the total synthetic crude through the cracking zone without separation of recycle stock and residuum.

As a result of the use of large reaction chambers, externally heated, the throughput of the units is small, not exceeding 2000 barrels per day for the latest Jenkins units. The effectiveness of the units is insufficient due to the low temperature of cracking. As a result of the circulation of the total synthetic crude, the extent of cracking is very moderate, owing to the coke-forming properties of the condensation products formed in cracking and recirculated through the cracking zone.

The principal common features of the cracking processes used commercially at the present time are as follows: (1) Heating of the charging stock takes place only in the continuous coil. (2) The use of high temperatures, from 480-600°C. (896-1112°F.), resulting in high efficiency of the process. (3) Reaction chambers are not heated and are used only for completing cracking, if at all, the total cracking being performed in tubes. (4) Only clean recycle stock, free from the heavy condensation products formed in cracking, is recycled through the cracking zone. The method of clean recirculation has been described in the patents of Dubbs,¹² Egloff,¹³ and Behimer.³

The pressure used in modern cracking units varies within broad limits, but units employing high or moderately high pressures of 250 lbs. per square inch gauge and higher predominate.

The high yields of cracked gasoline, large capacities and long operating cycles of modern cracking units could be obtained only by means of the aforementioned basic features.

The yields of gasoline and other cracked products in modern cracking processes have been given above (pp. 161-162). It should be emphasized that the final yields of gasoline depend mainly on the charging stock, and not on the process of cracking. The yields of gasoline in the vapor-phase

process, however, may be somewhat lower at the expense of larger gas formation as compared with the pressure process. The capacities of modern cracking units may be as high as 30,000 barrels of fresh stock per day. A continuous operating time of 3 months is common. The average cycle efficiency is usually from 90 to 95 per cent.

The direct consumption of fuel in modern cracking units does not exceed 5-6 per cent of the fresh charging stock.

The Holmes-Manley Process

This process is characterized by a long reaction time provided in a multiple-chamber arrangement set vertically, in which the number of chambers, of large diameter, may vary from four in the older design to two in the newer. The latest units of this process are of the internal recycling type, giving as final liquid products only naphtha and fuel oil. The description given here follows the flow chart (Figure 33).

The virgin gas oil charge is pumped through a coil heat exchanger at the top of No. 1 bubble tower, there contacting indirectly the stream of naphtha vapor and affording reflux for the tower. Leaving the exchanger, the gas oil is discharged into the bubble tower of the tar-stripping unit, where it combines with the recycle gas oil recovered from the pressure bottoms. This mixed charge is then pumped through the economizer section of the DeFlorez Upshot Heater. After leaving the economizer, the condensate from the base of No. 1 bubble tower is pumped into the stream and the combined mixed charge and condensate passes through the heating coil, discharging at a temperature of about 477°C. (890°F.) to the first of two 7 x 42-foot stills connected in series. In these reaction chambers a separation is made between liquid and vapor, the liquid being drawn from both stills so that no appreciable level is maintained. The naphtha vapor passes to No. 1 bubble tower and is fractionated, condensed, and discharged through the control house to storage. The stills, bubble tower and condensing system operate at approximately 400 pounds (27 atmospheres) pressure.

The liquid withdrawn from the stills, and known as pressure bottoms, is discharged to the tar-stripping equipment. In the evaporator section of this equipment the fuel oil is separated as a residuum and the vapor passed to the bubble tower section, where tar-stripper naphtha vapor and recycle gas oil are separated. The tar-stripper naphtha vapor is condensed and part of it is returned to the tar-stripper bubble tower as reflux. The remainder goes to storage and is eventually combined with the naphtha produced from No. 1 bubble tower. The flow of the combination of recycle gas oil and virgin gas oil has been traced.

The DeFlorez Upshot Heater has a vertical cylindrical furnace which has an internal diameter of approximately 18 feet, and is 28 feet high. A double row of tubes is arranged around the inner periphery of the furnace walls, the flow being through the outer row and then through the inner row. The furnace is fired from the bottom with gas. The products

of combustion pass from the top of the cylinder through a square section of reduced area, which contains the economizer. The economizer tubes are arranged so that the tubes in one horizontal row cross the tubes in the next row at a 90° angle. After leaving the economizer, the gas passes to an air preheater furnishing preheated air to the furnace, thence to a short stack mounted over the air preheater.

The operating period of this unit is approximately 400 hours per run and it is claimed that this operation time may be assumed to be 90 per cent or better if proper attention is given to cleaning and repairs, except when highly corrosive stocks are processed.

The Dubbs Process

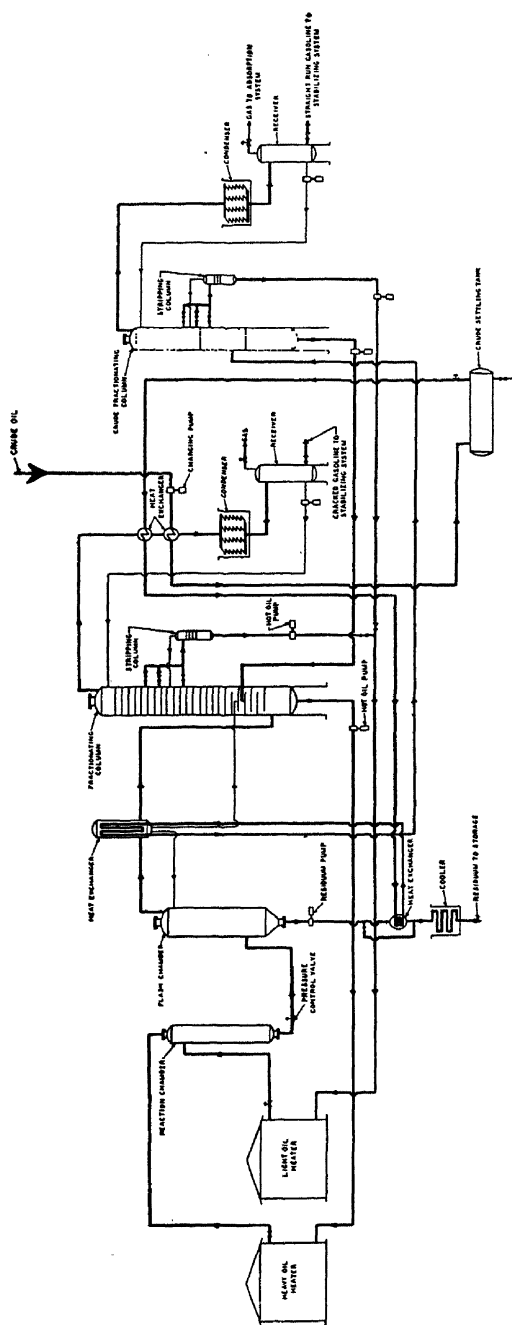
The Dubbs cracking units consist essentially of the heating coil in which the charging stock is heated to cracking temperatures, the reaction chamber into which the heated stock is discharged, the dephlegmator or bubble tower receiving vapors from the reaction chamber, and a final condensing apparatus. Reflux condensate formed in the dephlegmator or bubble tower is usually recycled through the heating coil. The entire system is operated under considerable pressure, usually of the order of 250 pounds per square inch gauge.

Residual type operation is carried out in a unit equipped with a flashing system, in which the volatile portions of the residuum are taken off by flashing the residuum into a chamber at lower pressure. In non-residuum operation the flash chamber is not employed and the coke is deposited in the reaction chamber or in special coking chambers.

Figure 34 represents a Dubbs selective cracking unit with two furnaces. The charging crude is pumped to the plant through heat exchangers and a crude settling tank to the crude fractionating column for straight-run distillation. The residuum from this column is pumped to the cracking fractionating column where it is diluted with heavy recycle stock and then passes to the heavy-oil furnace. The light distillates from the crude and cracking fractionating columns are charged to the light-oil furnace. The synthetic crudes from both furnaces pass into the single reaction chamber and then to the flash chamber, for the separation of cracked residuum and distillates.

The temperatures in the outlet from the heavy-oil heater vary from 470 to 500°C. (878 to 932°F.) and those in the outlet from the light-oil furnace may be as high as 525°C. (972°F.) or more. The same pressure is maintained in all parts of the cracking system except for flashing.

It should be mentioned that in the above scheme the synthetic crude is passed from the furnace to the top of the reaction chamber and leaves the chamber at the bottom. Thus the total synthetic crude is discharged into the flashing tower without separation. This full-flash operation differs from the customary operation of the Dubbs units largely used in the past, where the synthetic crude is separated in the reaction chamber



34.—Distilling

into residuum and distillates. The residuum alone is flashed in the flash tower, while the distillates are passed to the fractionating tower.

The Cross Process

The Cross units, unlike the Dubbs units, have an evaporator in which separation of the distillates from the heavy residuum takes place at lower pressures. The vapors are further separated in the rectifying column into gasoline and gas oil, the latter being used for recycling.

Figure 35 is a flow sheet of a Cross unit. The fresh charging stock to the unit is passed first, by means of a suitable pump, through partial condensers on the overhead vapor streams from the bubble tower and evaporator, respectively, to acquire heat before being introduced into either the bubble tower or the evaporator.

If the fresh feed is allowed to enter the bubble tower it is diluted on mixing with the intermediate gas oil or recycle stock accumulating in the base of the bubble tower.

The feed may be introduced into the evaporator where it is reduced to bottoms, the distillate content passing over into the bubble tower where it is condensed together with the recycle stock as charge for the cracking furnace.

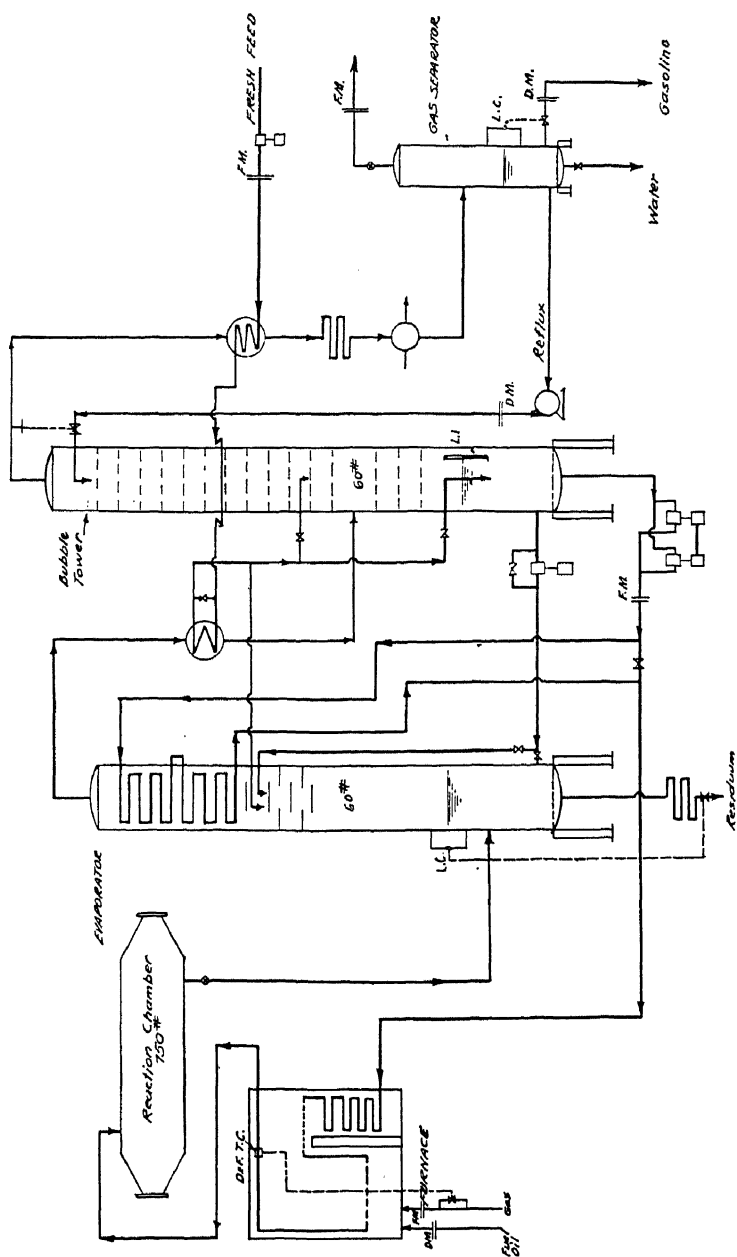
A high-pressure hot-oil pump takes suction from the base of the bubble tower and discharges the mixture of recycle stock and fresh feed first through a high-pressure spiral coil in the head of the evaporator before entering the Cross furnace itself.

This furnace is of the tubular type, in which the greater part of the heat input is transferred to the oil by radiation. The oil flows first through the preheater or convection section and then through the wall and roof tubes where it is heated to about 500°C. (932°F.) under a back pressure of 750 pounds (50 atmospheres). This hot oil is then directed into a reaction chamber, where it is held under 750 pounds pressure. In this chamber the cracking reaction begun in the furnace is completed.

The cracked mixture is withdrawn from the base of the reaction chamber and introduced into the evaporator, the pressure having been reduced to 60 pounds (4 atmospheres), under which pressure distillation and separation take place.

The quality of the fuel oil withdrawn from the base of the evaporator is determined by the temperature maintained at this point. Control of this temperature is effected by returning a portion of the gas oil from the base of the bubble tower into the evaporator for quenching. Ordinarily Cross units are operated for the production of a marketable "Bunker C." fuel oil.

The cracked gasoline and recycle stock vapors, together with the distillate from the feed if such is fed into the evaporator, pass overhead from the evaporator and enter a bubble tower for complete fractionation and separation into end point gasoline and gas oil recycle stock. The condensed gas oil accumulates in the tower bottoms at approximately



Courtesy The M. W. Kellogg Co.

FIG 35.—Cracking Process

315°C. (600°F.). The end point cracked gasoline vapors pass overhead from the bubble tower, and are subsequently cooled and condensed before entering a separator where the gases formed are removed overhead, while the cracked gasoline is drawn to storage.

The Cross unit is being employed extensively as a nucleus for a complete cycle of refinery operations on crudes, such as topping, viscosity breaking and cracking for ultimate yield of gasoline, all concentrated in one plant. The crude is preheated to a suitable temperature for vaporizing the straight-run gasoline and kerosene from the waste heat of the cracking plant. These straight-run products are removed in an auxiliary crude flash tower. The topped crude is then reduced by slight cracking to produce a relatively large quantity of gas oil charging stock and a low-viscosity fuel oil. Incidental to the yield of these products, a small amount of cracked gasoline is also obtained. The gas oil produced is charged to the Cross unit and cracked therein to an ultimate yield of gasoline and commercial fuel oil.

In these combination units the reaction chambers are frequently not used and are replaced by soaking tubes. As a result, the familiar conventional Cross system is rapidly losing its identity.

The Tube and Tank Process

The present-day Tube and Tank process belongs to the type which employ high pressures, from 750 to 1000 pounds per square inch gauge in soakers. The temperature of the cracking stock entering the reaction chamber is about 500°C. (932°F.). The old Tube and Tank units operated under lower pressures, from 250 to 300 pounds per square inch gauge in the soakers.

The layout of the latest Tube and Tank process described by Truesdell³¹ is shown in Figure 36. Fresh stock is passed by the cold pump through heat exchangers 1, 2, 3, 4, connected to the columns. The feed stock, so heated to 288°C. (550°F.), then enters the accumulator and is thence pumped by the hot pump through the high-pressure heat exchangers into the furnace. The feed temperature is brought up to 343°C. (650°F.) in these heat exchangers. Part of the heat of condensation of the vapors from the separator is used in these exchangers.

In the furnace the oil passes through the first coil of the convection section, thence through the radiant section and finally through the second part of the convection section, after which it enters one of the soakers. From the soaker the oil passes through the reduction valve into the separator, where a pressure up to 65 pounds is maintained.

Tar separates in the lower part of the separator while the vapors pass through the upper part into the high-pressure heat exchangers mentioned above. The vapors from these heat exchangers pass into two columns in succession. As can be seen from the drawing, fresh feed as well as recycling stock enters the accumulator. The bottoms from the lower end of the column may be recycled by means of a pump through

the convection section of the furnace and they are then recycled into the proper column for scrubbing.

As can be seen from this drawing, the Tube and Tank process, like the Cross process, is characterized by the high working pressure maintained only in the tubes and the chambers (if the high-pressure heat exchangers are disregarded). The reaction chambers are placed in a vertical position, but the evaporators (separators) are horizontal.

Cracking Processes without Reaction Chambers

Ten years ago the Winkler-Koch process was the only high-pressure cracking process, widely used commercially, which did not employ reaction chambers. A further development of the Winkler-Koch process in the United States has been hampered by patent litigation concerning the clean recycling used in the Winkler-Koch process. At the present time, in addition to the Winkler-Koch units, many other high-pressure cracking units do not use reaction chambers. The Kellogg and Lummus combination units without reaction chambers have been described in Chapter 2, (p. 139). The Winkler-Koch and Donnelly processes are described in this chapter.

Higher temperatures and a better control of temperature and reaction time are obtained in soaking tubes than in reaction chambers.

The Winkler-Koch Process

The temperature-pressure conditions of the Winkler-Koch process are about the same as those of the aforementioned processes performed under high pressures.

Figure 37 shows the layout of a Winkler-Koch unit equipped with

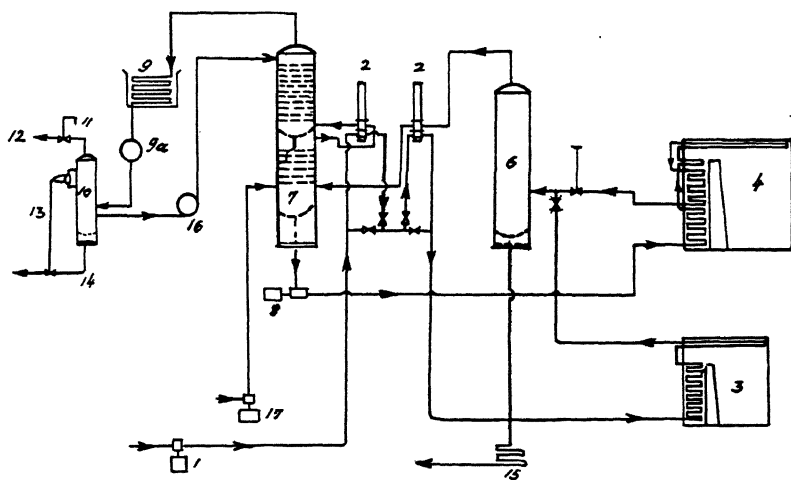


FIGURE 37.—The Winkler-Koch Cracking Process.

two furnaces, described by Kalita.¹⁸ The reduced crude is pumped by the cold oil pump (1) to heat exchangers (2) and then to the viscosity breaking furnace (3). From this furnace the charging stock passes to the evaporator (6) where it is blended with the synthetic crude from the cracking furnace (4). The distillates from the evaporator are passed to the tower (7) which separates pressure distillate from recycle stock. The recycle stock is pumped by the hot pump (8) to the cracking furnace (4). The temperatures and pressures of this process are given in Table 119.

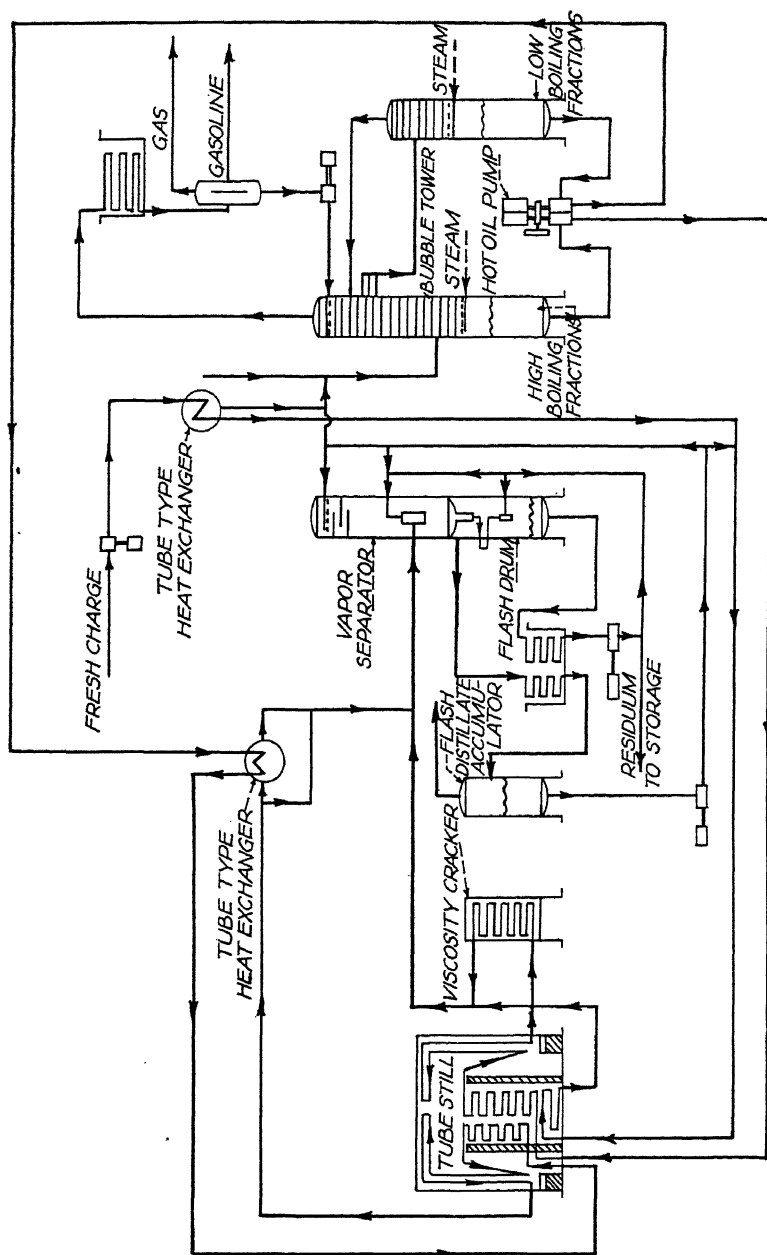
Table 119. Temperatures and Pressures of the Winkler-Koch Process.

Temperatures	°C. Temperature	°F.
Fuel oil outlet from first heat exchanger	198	388
Fuel oil outlet from second heat exchanger	322	612
Vapor inlet into first heat exchanger	250	482
Vapor outlet from first heat exchanger	226	439
Vapor outlet from second heat exchanger	354	671
Fuel oil at outlet of viscosity breaking furnace	383	721
Inlet into cracking furnace	321	610
Outlet from first section of cracking furnace	357	676
Outlet from second section of cracking furnace	400	752
Outlet from radiant tubes of cracking furnace	479	896
Outlet from soaking section of cracking furnace	490	914
Lower end of evaporator	404	760
Upper end of evaporator	405	761
Upper end of bubble tower	193	379
Pressure in Pounds per Square Inch		
Inlet of visbreaking furnace		110
Outlet of visbreaking furnace		93
Inlet of cracking furnace		600
Outlet of cracking furnace		400
In evaporator		33
In bubble tower		26
In gas separator		19

In the new Winkler-Koch cracking furnaces the temperature in the outlet from the soaking tubes exceeds 500°C. (932°F.).

The Donnelly Process

The Donnelly process widely uses the quenching process and blends the cracked products leaving the cracking coils. No reaction chambers are employed. The fresh feed (Figure 38) is pumped through a heat exchanger to the furnace and then to the vapor separator or evaporator. Before entering the vapor separator, the fresh feed is first commingled with cracked heavy recycle stock and then with cracked light recycle stock. It should be mentioned that the temperature of the cracked heavy recycle stock is higher than that of the cracked fresh feed, while the cracked light recycle stock has the highest temperature. The mixture of the above three cracked products enters the vapor separator for the separation of distillates from residuum. The temperature in the vapor separator is controlled by the quenching effected by the injection of residuum and flash distillate, as shown in the figure. The distillates from



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 38.—Flow Chart of the Donnelly Process.

the vapor separator are passed into the bubble tower and a supplementary tower, where they are separated into gasoline and two recycle stocks mentioned above. The heavy recycle stock is cracked at temperatures up to 925°F. and the light recycle stock at temperatures above 925°F. According to Donnelly's patent 2,052,340 (1936), the cracking of the light recycle stock may be carried out in vapor phase. The Carburol process, similar to the cracking processes without reaction chambers previously described is being used to a certain extent in European refineries.^{28a}

Vapor-phase Cracking Process

The general scheme of vapor-phase cracking is very similar to that of pressure units employing evaporators. Reaction chambers are not used in vapor-phase cracking due to the high temperatures and short cracking times which are the distinct features of the process in question. The operation of quenching is of paramount importance in the vapor-phase process. Insufficient quenching results in excessive coke formation.

The temperature of commercial vapor-phase cracking is 600°C. (1112°F.). The pressure in the outlet of the cracking coil is about 50-150 pounds per square inch, and the same pressure is maintained in other parts of the cracking units, *i.e.*, in the evaporator and bubble tower. The gasolines obtained under high-temperature conditions are high in aromatics and olefins and have very pronounced antiknock qualities. Besides these advantages, chief of which is that the process is operated at low pressure, vapor-phase cracking has many disadvantages which hamper its extension.

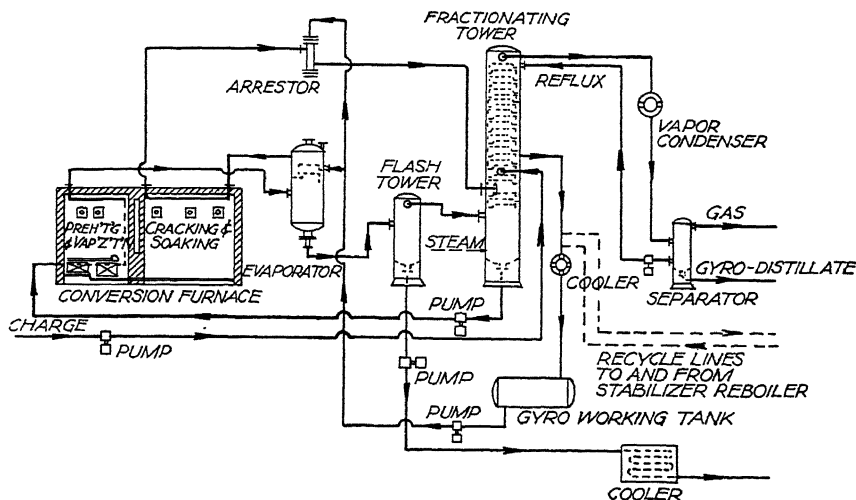
The heat transfer to the vapors offers great difficulty due to the low heat conductivity of the vapors under low pressures. The large sizes of the vapor-phase units constitute another drawback. The consumption of fuel is higher than in the pressure process. The formation of cracked gases, which amounts to as much as 25 per cent, is high. The yields of cracked gasoline are considerable and the coke formation is low, provided the velocity of the vapors is sufficiently high. Of course only kerosene and light gas oils can be treated in the vapor phase without excessive coke formation.

The vapor-phase cracking units operating in the United States belong to the following systems: Gyro, DeFlorez, Pratt and the True Vapor Phase process.

The Gyro Process

Gyro cracking is a typical vapor-phase process performed at as high a temperature as 593°C. (1100°F.) and under the low pressures of 75 to 100 pounds per square inch. The crude (Figure 39) is charged to the fractionating tower, where it is stripped of straight-run gasoline. The straight-run residuum blended with recycle stock is passed to the viscosity breaking and vaporizing furnace and then to the evaporator. The vapors from the evaporator are passed to the vapor-phase cracking furnace,

where the temperature of the charging vapors is increased to 1100°F. at the outlet. From the cracking furnace the vapors are conveyed to the arrester, and quenched by a light distillate produced in the fractionating tower. As a result of the quenching, the temperature of the cracked vapors decreases from 593°C. (1100°F.) to 380°C. (716°F.). The



Courtesy Oxford University Press

FIGURE 39.—The Gyro Process.

quenched vapors enter the fractionating tower for the conventional separation.

At present the Gyro units are purely thermal; iron oxide catalyst was used in earlier units.

The DeFlorez Process

The DeFlorez process is a high-temperature system in which the oil is raised in a heater to temperatures approximating 593°C. (1100°F.). It employs relatively low pressures which range from 100 to 150 pounds per square inch. As high a pressure as 500 pounds per square inch is used in the latest DeFlorez units, which should be considered rather as pressure or mixed-phase units.

Figure 40 shows the flow of oil through a typical DeFlorez unit. The cold charging stock is passed through a heat exchanger to the evaporator above the bubble trays. The distillation or stripping of the lighter fractions from the charging stock occurs in the evaporator, together with light cracking. The vapors evolving from this stripping and cracking action, as well as those of the vapor-phase cracked product, pass overhead from the evaporator and thence into the lower section of the bubble tower. The overhead products from the bubble tower, cracked gasoline

and gas, are withdrawn from the bubble tower through a cooler and condenser.

The lower section of the bubble tower serves as a reservoir for the accumulation of the clean condensate which is pumped to the furnace as feed stock. The residuum in the evaporator is conveyed to the flash tower. The process is used for residuum and non-residuum operations and for reforming.

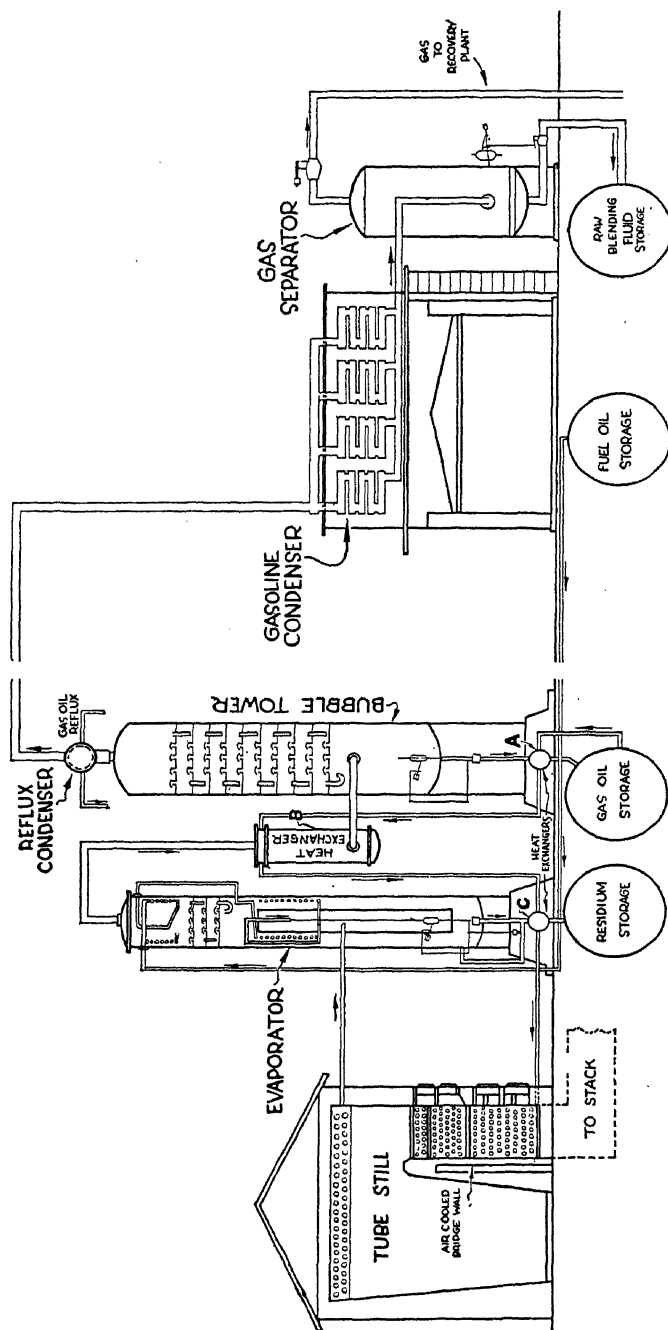
The Pratt Process

The Pratt process is similar to the vapor-phase processes discussed above. According to Foster,^{14a} the gas oil or recycle stock (Figure 41) is pumped through heat exchangers A, B, and C to the furnace, where it is heated to a temperature of 593°C. (1100°F.) or above. The cracked vapors enter the evaporator and are met by a stream of heavier stock, such as fuel oil, etc., which is pumped to the evaporator. Thorough contact between the cracked vapors and the heavy stock is an essential feature of the process. The heavy oil quenching the cracked vapors is distilled and cracked to a certain degree at the temperature of the evaporator. The cracked and uncracked vapors are passed into the bubble tower for further separation.

The True Vapor Phase Process

The True Vapor Phase or the Knox process is performed in the presence of an inert gas as the heat carrier. The flow diagram of the process is given in Figure 42. The cracking stock is pumped through heat exchangers, mixed with recycle stock, and the mixture heated in a vaporizer. From the vaporizer the mixture passes into a flash chamber at a temperature of about 482°C. (900°F.). The vapors from the flash chamber pass into the superheater coil where they are heated very rapidly to a temperature 11-22°C. (20-40°F.) below that at which they are cracked in the reaction chamber. The inert gas is first heated in a special coil up to 592°C. (1100°F.) and higher according to the cracking temperature desired. Two flows of the inert gas and preheated vapors from the superheater are mixed in the reaction chamber. The temperature in the reaction chamber may vary from 510 to 621°C. (950 to 1150°F.). It is usually kept close to 565°C. (1050°F.). The pressure in the reaction chamber may be from 50 to 135 pounds per square inch gauge. The amount of inert gas averages one pound per 3.5 pounds of the vapors to be cracked. From the reaction chamber the cracked vapors and gas are passed into a scrubber where gas, gasoline and recycle stock are separated from residuum. The gas, gasoline and recycle stock pass to the bubble tower and other parts of the unit for the further separation.

Praeger²⁷ gives the following results on the cracking of an East Texas gas oil in the True Vapor Phase process (Table 120). A comparatively moderate gas formation at more moderate temperatures should be mentioned. The octane number of cracked gasoline markedly increase with



Courtesy "National Petroleum News"

FIGURE 41.—Pratt Cracking Process.

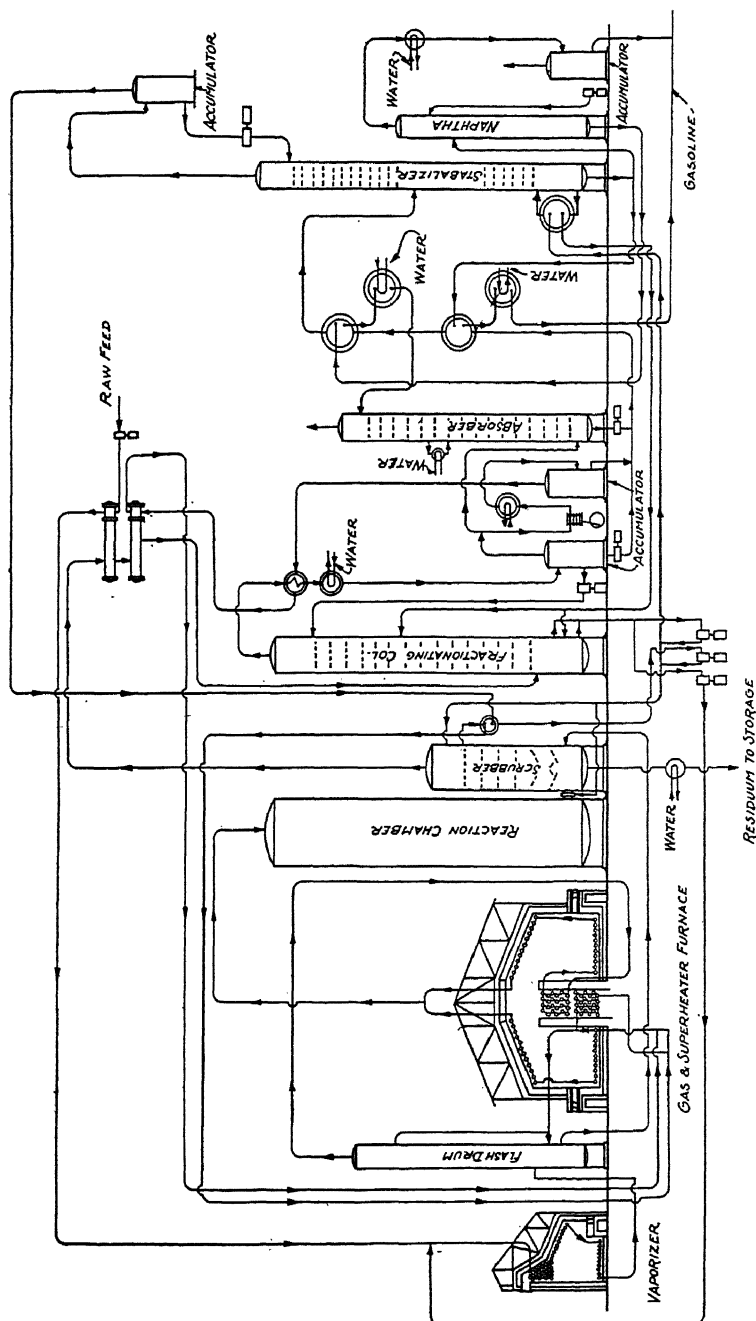


Figure 42.—True Vapor-phase Process.

Courtesy "National Petroleum News"

the temperature of the process. Another interesting feature is a high conversion per pass.

Table 120. Cracking of East Texas Gas Oil in the True Vapor-Phase Process.

Cracking Conditions	Yield by Volume			Loss and Gas (by wt.)
	Gasoline	Octane No.	Residuum	
1. Temperature 552°C. (1025°F.) Recycle Ratio 3.3 Conversion per pass 14%	65	69	20	16
2. Temperature 580°C. (1075°F.) Recycle Ratio 2.2 Conversion per pass 20%	58.5	71.3	23	20
3. Temperature 621°C. (1150°F.) Recycle Ratio 0.5 Conversion per pass 28%	50	74	28	26

Cracking or Distillation to Coke

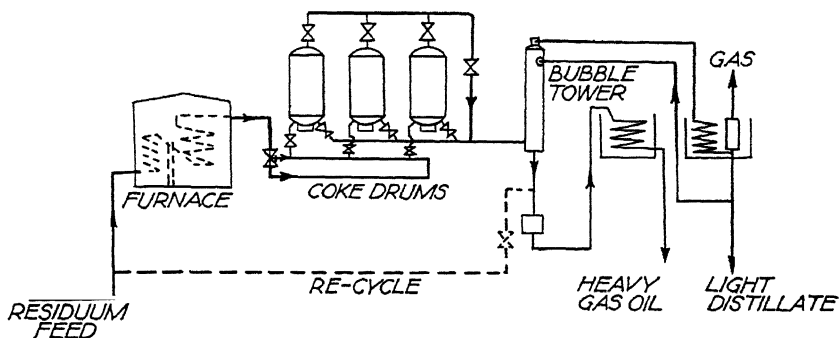
Cracking to coke, as the non-residuum cracking process, has been described in Chapter 2. Every cracking process discussed in this chapter can be transformed into a non-residuum process by the addition of coking chambers and eventually of a supplementary coking furnace (Figures 10 and 11).

In addition to the non-residuum process, destructive distillation to coke is another method of producing distillates and coke from petroleum products. The difference between these two methods, however, is quantitative rather than qualitative. As a matter of fact, the cracking reactions readily take place in destructive distillation, resulting in the formation of gas and cracked gasoline.

The destructive distillation of crudes and residues to coke, performed periodically in stills externally heated, was widely used in the past. This process, being expensive due to short working cycles and a large application of manual labor, is employed to a very limited extent at the present time. It may be considerably improved and perfected by separate heating of the charging stock in a conventional tube furnace and by further coking of the preheated charge in coking chambers without external heating, as is done in the non-residuum cracking process. This operation is of practical importance at present due to the overproduction of heavy residues. The residues processed in the continuous coking operation produce distillates and coke, more marketable products than heavy residues.

This process has been described by Diwoky⁹ as the Delayed Coking process, indicating that coke formation is delayed until the charging stock is introduced into the coking chamber. A simplified flow sheet of the process is given in Figure 43. The charging residuum is heated in a conventional heater to a temperature of about 488-496°C. (910-925°F.) and then enters a "circulating ring." The hot residuum flows around the ring in both directions, providing circulation of charging stock through the whole line and thereby eliminating the deposition of coke.

The preheated residuum is continuously discharged from the circulating ring into the bottom of one of three coking drums, until the drum is filled with coke. Three coking drums ensure continuous operation. Each coking drum is 16 feet in diameter and 35 feet in height, the daily capacity of the unit being about 3,000 barrels. The normal time of operation of each drum is 36 hours. When the drum is filled with coke, the hot feed



Courtesy "National Petroleum News"

FIGURE 43.—Delayed Coking Process.

is switched to the second drum. The first drum is allowed to stand for 24 hours (setting) in order to continue the decomposition; this results in increase in the hardness and decrease in the volatile constituents of coke. The drum is then cooled by steam and water and cleaned from coke. All operations and preheating of the cool drum for the next operation require 48 hours, the total cycle being 108 hours.

Operating data for the Delayed Coking process are given in Table 121. The yields of the products of the process are summarized in Table 122. The yields in the Delayed Coking process are close to those in the batch distillation to coke.

In contrast to the Delayed Coking process, the Knowles process, described by Albright,¹ uses external heating for coking. The heavy residuum is preheated in a conventional pipe-still to 466°C. (870°F.) and then conveyed to a battery of 4 or 6 Knowles ovens. The floors of the horizontal refractory-lined ovens are heated from below by burners in refractory combustion chambers provided with channels for the combustion gases. The preheated residuum is conducted to the oven floor. The charging time is about 2 hours. The temperature in the oven increases to about 815°C. (1500°F.) and then gradually decreases to 427°C. (800°F.) until the end of the coke-forming period. The coking time is 3 hours. The discharge of the coke is mechanical. The oven doors are opened by raising them with electrical hoists. An electrically driven ram moves the mass of coke from the floor into a special car, where the coke is immediately quenched by spraying with streams of water.

Table 121. Operating Conditions for Delayed Coking Unit.

Flows, bbls. per hour	
Residuum charge	119
Bubble tower condensate	80
Bubble tower net overhead	24.3
Bubble tower top reflux	27
Temperature (°F.)	
Residuum to furnace	685
Residuum to coke drums	910
Coke drum vapors	784
Bubble tower (bottom)	576
Bubble tower (top)	308
Furnace temperatures:	
Above convection section	1270
Leaving convection section	834
Pressures (lbs. per sq. inch gauge)	
Charge to furnace	160
Coke drums	3.8

The discharging time is 1 hour and 15 minutes, including sealing of the doors.

Table 122. Yields from Coking Mid-Continent Residuum (A.P.I. Gravity 19.0).

	Yield (% of Residuum)	
Gas	7.2 by weight	1.398 sp. gr.
Light distillate	20.4 by volume	53.6 A.P.I. gr.
Heavy distillate	67.2 " "	24.4 " "
Coke (dry)	12.4 by weight	
Yields Corrected to 400° C.E.P. Stabilized Gasoline		
Gas	4.5 by weight	
Gasoline	22.4 by volume	
Gas Oil	69.1 " "	
Coke	12.4 by weight	

A vapor-phase cracked residuum produces in the Knowles process 11 per cent gasoline, 55½ per cent light gas oil and 24 per cent coke (per cent by weight). As can be seen from the aforementioned data, the temperature used in the Knowles process is much higher than in the non-residuum cracking or in the Delayed Coking process.

The removal of coke from the reaction and coking chambers is an operation involving high labor and operating expenses. The cable method is the most generally used means of removing the coke. A steel cable is suspended in the reaction or coking chamber in the form of a flat coil. After the operation is over and the chamber is filled with coke, it is steamed and cooled with water. Then the bottom is valved off, and the cable is pulled with a hoist, at a rate of about 50 feet per minute. The coke is disintegrated by the cable and is discharged. A high yield of lump coke is an advantage of this method. On the other hand, the pieces of wire torn from the cable impair the quality of coke.

In another method of coke removal, a drill stem is introduced into the opened bottom head of the chamber, after the latter has been cooled with steam and water. The coke bed is bored by drilling in various directions and disrupted into lumps which are discharged from the chamber. A considerable yield of breeze is a disadvantage of the drilling method.

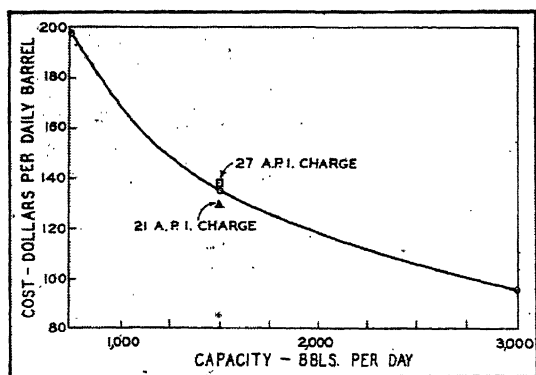
In both methods the final removal of coke from the chamber wall requires manual work under very severe temperature and humidity conditions.

A new hydraulic method of coke removal described by Court,⁸ uses water-jets under high pressure (about 1000 pounds per sq. inch gauge) for the disintegration of coke. After the chamber is cooled and opened, the first step is to bore a hole about 18 inches in diameter downward through the coke bed. The second step, cutting and disintegrating the coke, is carried out by the revolving water jets ejected from the nozzles of the apparatus, which is placed in the hole. This operation starts in the bottom section of the chamber and progresses to the top. The coke, cut into layers by the revolving jets and disintegrated, falls to the bottom of the chamber. The percentage of lump coke produced by the hydraulic method is comparable to that produced by the cable method. All coke is completely removed and manual finishing is eliminated.

The clean-out time for a 10 x 40-foot chamber is about 5 hours by the cable method, 4 hours by the drilling method and 2½ hours by the hydraulic method.

Cost of Cracking Plants and Operation

The cost of standardized mixed-phase cracking units depends mostly on their daily capacity, the choice of the process being of secondary importance. The cost of cracking units per barrels of daily capacity de-

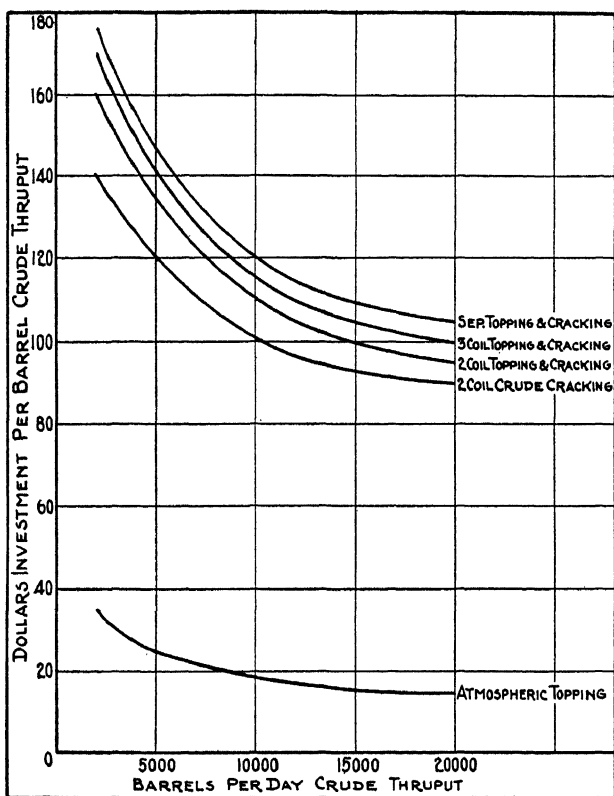


Courtesy "Oil and Gas Journal"

FIGURE 44.—Cost of Cracking Plants per Barrel Capacity (24 A.P.I. Charge Stock).

creases substantially with increasing total capacity. According to Nelson,²⁵ the relationship between the cost per barrel of daily capacity *versus* total capacity for distilled-oil recirculation cracking units is represented by Figure 44. Thus the cost per barrel per day decreases from about \$200

for a small unit of 750 bbls. daily capacity, to \$96 for a larger unit of 3000 bbls. daily capacity. These figures relate to the plants operating on a 24° A.P.I. Mid-continent reduced crude. The first cost depends to a certain degree on the A.P.I. gravity of the charging stock. The plant cost increases when processing higher A.P.I. gravity reduced crude oils, owing to higher yields of gas oil for cracking and larger cracking coils. The difference in the cost, however, is not very significant. Nelson²⁵



Courtesy "National Petroleum News"

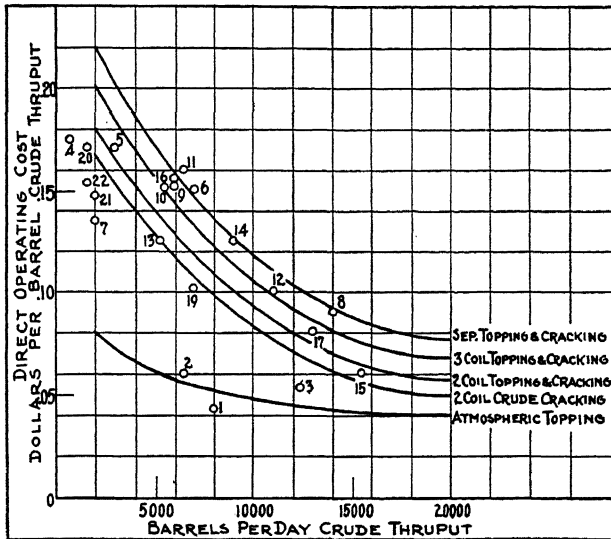
FIGURE 45.—Cost of Combination Units per Barrel Capacity.

gives the total cost of a cracking plant of 1,500 bbls. daily capacity as \$195,049, when processing 21 A.P.I. gravity reduced crude, and \$200,643 for the same capacity when processing 27° A.P.I. gravity reduced crude.

The aforementioned figures of the cost per barrel per day, as well as of the total costs, include all expenses connected directly with cracking and do not include investments on the ground, tank farm and generation of power required for the cracking operation.

The cost of operation of mixed-phase cracking plants, given by Nelson, is indicated in Table 123. An average operating cost is between 37 and 43 cents per barrel of charging stock for the daily capacity of 1,500 barrels. It is appreciably lower for higher capacities, particularly for combination units not exceeding 20 cents per barrel.

The economics of combination units is demonstrated by the data of Smoley.³⁰ Figure 45 represents the cost of investment and Figure 46



Courtesy "National Petroleum News"

FIGURE 46.—Direct Operating Costs of Combination Units.

the direct operating cost per barrel of daily capacity. The initial cost as well as the direct operating cost is lower for all types of combination units (3 and 2 cracking coils) as compared with separate topping and

Table 123. Cost Balance of Cracking Plant Operation (1500 bbls.).

	V	I	II	III	IV
Capacity (bbls./day reduced crude)	750	1,500	1,500	1,500	3,000
Gravity of charge stock (A.P.I.)	24	21	24	27	24
Value of charge stock (cents per bbl.)	55	50	55	60	55
Cost of plant	\$148,908	\$195,049	\$203,310	\$206,643	\$288,816
Value of products, per year					
Raw gasoline at 4 cents/gallon	\$218,000	\$395,000	\$436,500	\$478,000	\$860,000
Fuel oil at 50 cents/bbl.	62,500	141,000	125,000	109,300	250,000
Total	\$280,500	\$536,000	\$561,500	\$587,300	\$1,110,000
Cost, per year					
Operation*	\$123,000	\$202,000	\$223,400	\$242,500	\$420,000
Value of charge stock	151,000	274,000	302,000	330,000	604,000
Total	\$274,000	\$476,000	\$525,400	\$572,500	\$1,024,000
Profit					
Dollars per year	\$6,500	\$60,000	\$36,100	\$14,800	\$86,000
Cents per barrel charge	2.4	10.9	6.6	2.7	7.9

* Supervision and labor \$63 per day for all plants or 4.2 cents per barrel based on 1,500-bbl. charge. Heat, power, etc., 12 cents per barrel of stock charged to furnace. Depreciation and fixed charges, 6 per cent interest retired in 10 years.

cracking. The difference is particularly great for the operating cost, amounting from 1 to 4 cents per barrel depending on the type of combination unit. The curves clearly show the advantages of high-capacity combination units, exceeding 10,000-15,000 barrels per day.

Statistics on Cracking

The development of cracking in the United States may be seen from Table 124, in which the figures for the total crude oil and cracking capacities are given for years 1925-1938. The cracking capacity in 1938 and 1939 is about 55 per cent of the crude oil capacity.

The part played by cracked gasoline in the production of motor fuel is shown by the data of Table 125. During the last three years, the production of cracked gasoline has exceeded that of straight-run gasoline. The economic significance of these figures is obvious.

The latest recapitulation of cracking plants by types of process was made by the Bureau of Mines for 1937 (Table 126). Since 1937 the recapitulation of cracking plants by types is excluded from the information circulars of the Bureau of Mines due to the construction of new units which frequently combine parts of several types of process.

Table 124. Total Crude Oil and Cracking Capacity of Refineries in the United States.

Year	Total Crude Oil Capacity per Day (bbls.)	Total Cracking Capacity (bbls. per day)
1925	2,864,842	832,692
1926	2,858,467	940,090
1927	3,122,007	
1928	3,272,380	1,288,000
1929	3,608,540	1,476,874
1930	3,802,785	1,708,940
1931	3,987,685	1,950,781
1932	4,023,328	2,046,981
1933	3,921,055	2,031,395
1934	3,962,667	2,149,664
1935	4,072,400	2,229,269
1936	4,163,946	2,240,768
1937	4,376,081	2,355,070
1938	4,373,701	1,019,031*
1939	4,650,805	1,043,679*

* In terms of cracked gasoline production.

Table 125. Production of Motor Fuel in the United States.*

	1933	1934	1935	1936	1937	1938	1939
Straight-run	195,622	206,486	219,280	231,344	251,624	245,418	260,463
Cracked	180,623	182,433	207,537	239,650	268,136	270,471	295,142
Natural gasoline	29,319	33,435	39,333	42,770	39,177	50,317	49,896
Benzol	1,368	1,600	1,871	2,502	2,790	1,699	2,440
Total	407,932	423,454	468,021	516,266	571,727	567,905	607,941

* 000 omitted.

As the statistical data of Table 126 show, the older cracking processes, using the modified batch process, such as Fleming and Jenkins, are practically out of use. A slow development, or rather a certain regression of

Table 126. Recapitulation of Cracking Plants by Types of Process (January 1, 1937).

Type of Process	Cracking Capacity, bbls./day			Total
	Operating	Shut down	Building	
Biddison-Boyd	4,000			4,000
Black	16,000			16,000
Burton		7,000		7,000
Clark		500		500
Cross	194,000	14,750	15,250	224,000
DeFlorez	40,000			40,000
Doherty	28,800	1,000	1,200	31,000
Donelly	40,700	1,500		42,200
Dubbs	353,200	51,200	23,770	428,170
Fleming	3,000			3,000
Gyro	21,800			21,800
Holwes-Manley	280,500	1,800		282,300
Jenkins	3,500	17,700		21,200
Kellogg	49,500		31,000	80,500
Knowles	1,200			1,200
Link	37,000	7,250		44,250
Lummus		2,000		2,000
McKee	1,000			1,000
Own	532,250	9,700	53,000	594,950
Pratt	3,400			3,400
Richmond	3,700			3,700
Rowsey	1,000			1,000
Skelly-Rittman		4,000		4,000
Solar	4,000			4,000
True vapor phase	1,500	6,500		8,000
Tube and Tank	404,775	13,625	14,000	432,400
Wade		1,000		1,000
Winkler-Koch	52,500			52,500
Total	2,077,325	139,525	138,220	2,350,070

vapor-phase cracking, is another interesting feature of Table 126. The total operating capacity of the vapor-phase cracking units (DeFlorez, Gyro, Pratt, True Vapor Phase) is 66,700 barrels per day, or 3.2 per cent of the total operating capacity.

The rapid progress of the combination units is not clearly seen from Table 126. A part of the units in building, particularly the Kellogg units, belong to this type of cracking installation. The growth of the combination units is illustrated by the following figures relating to the crude capacity of the units in the United States:

1936	95,000 bbls./day	
1937	370,750 "	"
1938	445,050 "	"
1939	635,500 "	" 14b

The development of the Houdry catalytic process in 1938-1939 should be mentioned as another feature in the general development of cracking, as well as that of the thermal and catalytic conversion of gases. The total number of gas polymerizing and converting units in operation and construction is about 50. The total number of Houdry units in operation and under construction is fourteen, having a daily capacity of about 150,000 bbls.

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Chapter 5

Cracked Gasolines

Physical Properties

This chapter is confined to the properties of cracked and other synthetic gasolines. The properties of hydrogenated gasolines have partially been discussed in Chapter 3.

The specific gravity of cracked gasolines of end point 204°C. (400°F.) varies from 0.720 to 0.820 at 15°C. (from 65.0 to 41.1 A.P.I. at 60°F.) depending on the charging stock and the method of cracking. Cracked gasolines of a low specific gravity (around 0.725) are obtained in the mixed-phase cracking of light paraffin base products, while asphaltic and naphthenic charging stocks give, when cracked, gasolines of a higher specific gravity (0.750-0.760). The vapor-phase-cracked gasolines produced from the same charging stock are heavier as compared with those cracked in the mixed-phase process due to a larger content of aromatic hydrocarbons. Their specific gravity is as high as 0.770-0.780. The specific gravity of hydrogenation gasolines is about 0.720, when the process is performed at moderate temperatures, and about 0.800, when the temperature of the process is 500°C. or higher. Gasolines produced by the thermal conversion of gases, rich in low-boiling fractions, have a low specific gravity of about 0.720. The specific gravity of polymerized gasolines is somewhat higher.

The sharp and unpleasant odor of untreated cracked gasolines is caused mostly by the presence of mercaptans and some diolefins. The cracked gasolines from charging stocks high in sulphur have a particularly unpleasant odor. The odor of cracked gasolines becomes commercially sweet after the removal of sulphur compounds and diolefins by the conventional methods of treatment.

The color of highly purified cracked gasolines is water white, better than 30 Saybolt units. The yellowish color of untreated or aged cracked gasolines depends on the presence of some oxidation products, usually in minute quantities. The qualities of gasoline as motor fuel are not affected by discoloration. The color standard for motor gasoline was discontinued in 1927 and at present does not play an important part in the manufacture of cracked gasolines. In addition, the use of dyes in many commercial gasolines makes heavy treatment of cracked gasolines to obtain water-white color unnecessary.

Fractional Composition

The fractional composition of cracked gasolines is more or less similar

for gasolines produced in the mixed- and vapor-phase processes. The distillation curve is close to that of the U. S. Government specifications for motor gasoline, with some excess of low-boiling fractions. Hydrogenation gasolines produced at moderate temperatures are very rich in low-boiling fractions. On the contrary, highly aromatic vapor-phase-cracked gasolines, as well as high-temperature hydrogenation gasolines, are deficient in low-boiling fractions due to the accumulation of comparatively high-boiling aromatic hydrocarbons. Catalytically polymerized gasolines, and those produced by thermal conversion of gases, have a high content of light fractions.

The results of A.S.T.M. distillation of various cracked gasolines are summarized in Table 127.

Table 127. A.S.T.M. Distillation of Various Cracked Gasolines.

	Mixed- Phase	Vapor- Phase	Cata- lytic*	Thermal Conver- sion of Gases	Catal. Polym. of Gases	Moder- ate Temp. Hydro- gen	High Temp. Hydro- gen	Motor Fuel L	U. S. M. G.
A.P.I. Gr. at 60°F.	58.5	52.0	63.8	64.8	60.2	62.3	42.7		
Sp. Gr. at 15°C.	0.745	0.771	0.724	0.721	0.738	0.730	0.812		
I.B.P. (°F.)	102	90	108	93	100	85	102		
5%				111					
10%	158	138	144	117	132		168	max. 158.	max. 167
20%	191	165	157	122	151	148	214		
30%	210	188	170	133	162				
40%	239	212	186	144	176		300		
50%	266	237	200	154	201	234		max. 257	max. 284
60%	291	266	213	172	219		364		
70%	319	302	225	199	250	292			
80%	348	343	239	243	285				
90%	370	390	260	324	330			max. 356	max. 392
95%				412					
E.P.	394	436	320	487	416	406	425		

* Aviation gasoline.

The vapor pressure of cracked gasolines depending on the content of low-boiling fractions is not significant and can be made to order by stabilization of raw cracked gasolines in conventional stabilizers.

Chemical Composition

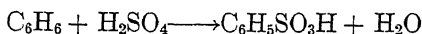
Cracked gasolines consist predominantly of paraffins, unsaturates, naphthenes and aromatic hydrocarbons. The total relative amount of oxygen and sulphur compounds in cracked gasoline does not exceed 0.01-1.0 per cent, the latter figure being rather exceptional. The oxygen and sulphur derivatives present in cracked gasolines will be discussed in separate sections.

There are no reliable commonly used methods of determining the above-mentioned constituents of cracked gasolines. The figures of the content of various hydrocarbons in cracked gasolines may vary to an appreciable extent depending on the method used. The most reliable methods of determining the chemical composition of cracked gasolines are discussed below.

Determination of the Total Content of Unsaturation and Aromatics

Unsaturated and aromatic hydrocarbons, under suitable conditions, can be quantitatively removed from paraffins and naphthenes by reaction with sulphuric acid. This method may be used for determining the total content of unsaturated and aromatic hydrocarbons in cracked gasolines.

Aromatic hydrocarbons of gasolines react with sulphuric acid forming sulphonics acids, which are soluble in an excess of sulphuric acid and are removed in the sludge:



The influence of the concentration of sulphuric acid on the reaction with benzene and toluene is well illustrated by the data given in Table 128. Thus toluene is more easily absorbed by sulphuric acid than benzene. The behavior of such derivatives of benzene as xylenes, ethylbenzene, etc., is similar to that of toluene.

Table 128. Treatment of 20-Per Cent Solutions of Benzene and Toluene in Gasoline Fractions of Similar Boiling Points with Sulphuric Acid of Various Concentrations.

Conditions of treatment: for the benzene mixture, two volumes of acid, and shaking for 2 hours; for the toluene mixture, one volume of acid, and shaking for 1½ hours.

Concentration of H ₂ SO ₄ mono-hydrate	Benzene absorbed Per Cent	Toluene absorbed
90	0.9	4
91	2.7	12
92	5.2	15.3
93	8.9	19
94	15.1	20
95.6	17.6	20

Completely substituted derivatives of benzene, as, for example, hexamethylbenzene which does not have any hydrogen in the benzene ring, cannot be subjected to the usual sulphonation reaction. Thus hexaethylbenzene is stable toward sulphuric acid to such a degree that it even can be recrystallized from fuming sulphuric acid. It should therefore be kept in mind that methods based on the sulphonation reaction do not make possible the determination of the quantity of the above aromatic hydrocarbons. These hydrocarbons could be determined in the hydrocarbons remaining after sulphuric acid treatment by the method of selective solubility by the use of the liquid sulphurous acid, aniline or some other suitable solvent. However, because of their boiling temperatures, these hydrocarbons would be present only in kerosene fractions.

Further experiments showed that two or three volumes of 94-98 per cent sulphuric acid remove quantitatively all aromatic hydrocarbons from gasolines. Fuming sulphuric acid, even with a small amount of free anhydride, should not be used, as it reacts vigorously with the other classes of hydrocarbons, particularly with naphthenic hydrocarbons; for this reason, excessive figures for aromatics are obtained.

Unsaturates react with sulphuric acid in various ways, forming sulphuric acid esters, alcohols, polymers and gums. The reactions will be discussed in detail in Chapter 6. A part of the products formed, soluble in sulphuric acid, is removed in the sludge, as well as sulphonic acids. Other products of the reaction between sulphuric acid and unsaturates, dialkylesters and polymers, are insoluble in sulphuric acid and are dissolved in treated gasoline. The boiling range of these compounds is higher than the final boiling point of the original gasoline. Thus, the high-boiling products formed can be separated by redistillation of the treated gasoline up to the end point temperature which the gasoline had before the treatment. The bottoms of redistillation represent the high-boiling products formed as a result of the treatment of unsaturates with sulphuric acid. Some dimers may boil in the range of the original gasoline, as for instance dibutene or dipentene, but they can be polymerized further to high-boiling polymers. If the polymerization of olefins to high-boiling polymers is complete, the iodine number of the treated and redistilled gasoline should be zero.

The influence of the concentration of sulphuric acid upon the reaction with olefins is demonstrated by the data of Table 129. A fraction having

Table 129. Action of Sulphuric Acid of Various Concentrations on the 50-100°C. Fraction of Products Obtained After Cracking Paraffin Wax.

Treating conditions: One volume of sulphuric acid; shaking for 30 minutes with cooling.

% Concentration of Sulphuric Acid as H_2SO_4	Iodine No. of Fractions After H_2SO_4 Treatment and Distillation	% Unsatur Remove
Original fraction	153.2	0.0
80	77.7	49.3
85	24.1	84.3
85 (repeated treatment)	13.9	90.9
90	1.4	99.1
95.6	0.17	99.9
Fuming	0.07	100.0

a boiling range of 50-100°C., produced after cracking paraffin wax and containing about 50 per cent olefins, was treated with sulphuric acid of various concentrations. The reaction of 80-85 per cent sulphuric acid with olefins is incomplete. Only 90-95 per cent acid completely removes olefins.

Attention should be paid to the reaction of the mixture of aromatics and unsaturates with sulphuric acid. If unsaturated hydrocarbons are present together with aromatics, a sulphuric acid of a concentration which would not react with aromatics as such, might react on them in such a mixture. Experiments conducted by Brochet⁶ show that unsaturated hydrocarbons are condensed with aromatics in the presence of sulphuric acid. Later experiments by Brame⁴ show that 85-per cent sulphuric acid absorbs about 30 per cent of aromatic hydrocarbons in the presence of unsaturated hydrocarbons, while 88-per cent acid absorbs even more than 50 per cent of the total of aromatic hydrocarbons present.

Tilicheyev and Massine⁴⁴ showed that sulphuric acid removes aromatic hydrocarbons much more energetically if unsaturated hydrocarbons are present, as can be seen from Table 130.

Sulphuric acid of 90 per cent strength removed only 3 per cent of the total of aromatics present when unsaturates were absent. But in the presence of unsaturates, 50 per cent of aromatics was removed. A 94-per cent sulphuric acid removed in the first case 10 per cent and in the second case 88 per cent of the aromatics present, etc. It is evident from

Table 130. Removal of Aromatic Hydrocarbons with Sulphuric Acid in Presence and Absence of Unsaturated Hydrocarbons.

Concentration of Sulphuric Acid (%)	Wt. of Aromatic Hydrocarbons Removed	
	In Absence of Unsaturates (%)	In Presence of Unsaturates (%)
90	3	50
94	10	88
98	27	100

Note: The treatment was carried out at 0°C.

this that it is quite impossible to select a sulphuric acid of a concentration which will remove the unsaturated hydrocarbons completely without simultaneously attacking the aromatic hydrocarbons. Thus 90-per cent sulphuric acid absorbs about 60 per cent of the total aromatics present, although it is not strong enough to absorb completely all the unsaturates at 0°C.

If the selective removal of unsaturated hydrocarbons by sulphuric acid is impossible, this reaction, however, can be used for determining the total content of unsaturates and aromatics. One volume of a cracked gasoline is treated with 3 volumes of 94-98-per cent sulphuric acid for one hour. The loss of gasoline after the treatment is recorded. The treated gasoline, after washing and neutralization, is distilled up to the end point of the original gasoline, in order to determine the amount of high molecular weight polymers formed. The total amount of unsaturates and aromatics equals the loss after the treatment with sulphuric acid plus the amount of the bottoms after the redistillation, recalculated on the corrected amount of the gasoline left after the treatment. The distillation residue of the original gasoline is subtracted from the amount of the bottoms. The iodine number of the redistilled gasoline must be zero or very small, indicating the complete removal of unsaturates.

Kattwinkel²⁶ removes aromatics and unsaturates by the mixture of phosphoric anhydride and sulphuric acid (30 grams of phosphoric anhydride are dissolved in 100 cc. of concentrated sulphuric acid). One volume of cracked gasoline is treated with three volumes of the mixture. The results do not differ from those obtained by the previously described treatment with three volumes of sulphuric acid. Kattwinkel's method gives better results for the products containing a large proportion of difficultly sulphonatable benzene, which is almost absent in cracked gasolines.

The products containing an excess of unsaturates are to be redistilled after the treatment with phosphoric anhydride-sulphuric acid.

By the method of Garner²³ unsaturated and aromatic hydrocarbons are removed with the aid of fuming nitric acid. The procedure is carried out at -10°C . by gradually pouring 50 cc. of the gasoline into 125 cc. of fuming nitric acid which has been previously cooled to -10°C . The mixture is continuously shaken during the addition. After the final addition and shaking the spent nitric acid is separated. The gasoline is then washed three times with 20 cc. of fuming nitric acid with a vigorous shaking in order to remove any dissolved nitro-compounds. After the separation of nitric acid, the gasoline is washed thoroughly with soda solution and water for determination of the aniline point. The volume of the treated gasoline is measured before the washing with soda solution. The difference between the original volume of the gasoline (50 cc.) and that after the treatment equals the total amount of aromatics and unsaturates present in the cracked gasoline.

Determination of Unsaturates

Many difficulties are involved in the selective determination of aromatics and unsaturates in cracked gasolines. Some aromatic as well as naphthenic rings may be combined with unsaturated radicals, and in this case the separation of aromatics and unsaturates is impossible by any means. It is believed, however, that almost all unsaturated hydrocarbons of cracked gasolines, at least of the mixed-phase process, belong to open chain olefins and to a lesser degree to cyclic olefins.

Application of the "ring analysis" (Waterman) to cracked gasolines containing unsaturates does not give comprehensive results. The percentage of paraffinic chains determined by this method for cracked gasolines includes the total percentage of paraffins, straight-chain olefins, and paraffinic and olefinic side chains. From the practical standpoint, the determination of unsaturates and other classes of hydrocarbons in cracked gasolines should be preferred to the determination of rings and open-chain constituents.

Most of the methods of selective determination of aromatics or unsaturates do not give satisfactory results, if both aromatics and unsaturates are present in the product. The action of sulphuric acid has been discussed in the previous section. The nitration method for the separation of aromatics is unreliable for cracked gasolines containing a comparatively small percentage of aromatics due to the solubility of nitro-compounds in gasoline. Faragher *et al.*¹⁸ use five equations for calculation of the percentage of aromatics on the basis of the volume of nitro-compounds produced, which varies with the concentration of aromatics in the mixture.

The removal of olefins with mercury acetate is very incomplete, particularly for higher fractions of gasoline. The use of aluminum chloride for the selective removal of unsaturates is not sufficiently selective, since this reagent is very reactive and attacks other hydrocarbons.

Kattwinkel²⁶ suggested removing the olefins selectively by sulphuric acid containing 5 grams of boric acid per 100 cc. of sulphuric, which would not attack aromatic hydrocarbons. According to Wells and Hedrick,⁵⁸ however, this method does not produce reliable results.

In spite of the severe criticism of the bromine or iodine number method (number of grams of halogen reacted with 100 grams of gasoline), this may give a fairly satisfactory estimation of the content of unsaturates in cracked gasolines. The calculation involves the molecular weights of olefins. If the bromine or iodine numbers are known for the narrow fractions of a gasoline, the molecular weights of the unsaturates may be accepted as equal to the average molecular weight of the fractions with sufficient accuracy. There are many modifications of determining the iodine and bromine numbers; those of Hanus and Francis²¹ are widely used for gasolines and give reproducible and reliable results. Richter,⁴⁰ after making a comprehensive study of various modifications, recommended the Hanus method.

The percentage of unsaturates calculated from the bromine or iodine numbers is subtracted from the total percentage of unsaturates and aromatics, and this gives the percentage of aromatics. The accuracy of this method is not very high, and the deviations from the actual figures may be as high as 3-4 per cent.

Moore and Hobson³⁴ and later Tilicheyev and Massine⁴⁴ developed the method of determining aromatics and unsaturates on the basis of the aniline points of cracked gasoline before and after the total removal of aromatics and unsaturates. Tilicheyev and Massine determined the aniline factors for olefins by preparing synthetic mixtures from pure unsaturates separated from cracked fractions (Table 131).

Table 131. Aniline Factors for Aromatics and Unsaturates.

Boiling Range of Fraction (°C.)	Aniline Factors*—	
	For Unsaturates	For Aromatics
65-95	2.3	1.1
95-122	2.4	1.2
122-150	2.8	1.2
150-200	2.7	1.5

* The depression in the aniline point effected by unsaturates (or aromatics) multiplied by the aniline factor or coefficient gives the content of unsaturates (or aromatics) in the fraction.

The total of aromatics and unsaturates was determined by the Kattwinkel method. The amount of unsaturates was calculated by the following equation:

$$Y = \frac{K_2(S - DK_1)}{K_2 - K_1},$$

where

Y = amount of unsaturated hydrocarbons in per cent by weight,

K_1 = aniline factor for the aromatics,

K_2 = aniline factor for the unsaturates,

S = total of aromatics and unsaturates,

D = increase in the aniline point after the removal of unsaturates and aromatics.

Garner²³ calculates the percentage of unsaturates and aromatics in cracked gasolines on the basis that the unsaturates lower the aniline point approximately 2/5 of the extent produced by the same percentage of aromatic hydrocarbons. As in the previous method, the aniline points are determined for the original cracked gasoline and for the gasoline freed from aromatics and unsaturates.

Selective Removal of Unsaturates

The methods of selective removal of unsaturates developed during recent years give more reliable results than those based on the bromine and iodine numbers or aniline points. Faragher, Morrell and Levine¹⁸ remove unsaturates selectively with sulphur monochloride. The sample of cracked gasoline reacts with sulphur monochloride, which attacks only unsaturates at room temperature. After the reaction is completed, the product is treated with a solution of sodium hydroxide, and is then washed and dried. The product obtained is then distilled at atmospheric pressure, and further under vacuum, to bring about separation of unsaturates-sulphur monochloride reaction products. Checking the method against mixtures having known quantities of olefins and aromatics gives excellent agreement between the actual and determined quantities of olefins. The idea of this method is very close to that of the bromination method developed by Tilicheyev and Massine.

According to these authors, the reaction between bromine and unsaturates of cracked gasolines takes place quantitatively at low temperatures of about $-20^{\circ}\text{C}.$, while, under these conditions, aromatics are not attacked by bromine. The dibromides formed are separated by distillation. The method is applied to the narrow fractions of gasolines.

The cracked gasoline under investigation was distilled with a fractionating column into the following fractions: below $60^{\circ}\text{C}.$, $60-95^{\circ}\text{C}.$, $95-122^{\circ}\text{C}.$, $122-150^{\circ}\text{C}.$, $150-200^{\circ}\text{C}.$ and the residue boiling about $200^{\circ}\text{C}.$

To determine the approximate chemical composition of the cracked gasoline, the iodine number is determined first by the Hübl-Waller method for each fraction separately (except the fraction boiling below $60^{\circ}\text{C}.$) and the approximate total content of aromatics and unsaturates is determined by the Kattwinkel method.

The approximate amount of unsaturates present in the given fraction is calculated by the iodine number. The difference between the total of aromatics and unsaturates determined by the Kattwinkel method and the amount of unsaturates gives the approximate content in aromatics. These preliminary tests are indispensable for the analysis to follow.

For the purpose of determining aromatic hydrocarbons (the method is described later) it is essential that the content of unsaturates be not over 20 per cent and that of aromatics not over 7 per cent. If more unsaturates and aromatics are present, the fraction is diluted with an

equal, double or triple amount of the fractions which were previously freed from aromatics and unsaturates. These fractions should have approximately the same final boiling points as the fractions under test. The dilution with the gasoline should be such as to give a mixture containing no more aromatics and unsaturates than specified above.

The total of aromatics and unsaturates present in each of the above fractions is then determined by a more accurate method. One hundred and fifty cc. of 98-per cent sulphuric acid is admitted into a separating funnel provided with a tight stopper and the whole is weighed to within 0.1 gram. Fifty cc. of the fraction under test is then carefully added to the sulphuric acid, by letting the gasoline run down the walls of the funnel. The funnel containing the mixture is then weighed again. This is the manner in which the amount of the fraction used in the investigation is determined. The funnel containing the mixture is placed for 15 minutes in a mixture of ice and water and then carefully shaken in the container with ice. As soon as no more heat is generated, the funnel is removed from the ice container and the mixture is shaken energetically for 30 minutes. After agitation the funnel is weighed again. Losses due to evaporation should not exceed 0.1 gram. The reaction mixture is then allowed to stand over night. The sulphuric acid used is carefully drawn off the next morning. The fraction is discharged through the upper part of the funnel and without any further treatment first into a beaker with a ground stopper, to allow the last drops of the sulphuric acid to settle; after this operation the fraction is finally discharged into a weighed round bottom .50-cc. flask. The flask with the fraction is weighed again, thus determining the weight of the fraction left after the sulphuric acid treatment. The product is then distilled with a proper fractionating column. In this operation the temperature observed in the vapors is usually 2 to 40°C. higher than the actual final distilling point of the fraction, *i.e.*, corresponding to 95°C., 122°C., etc. The more completely the product was settled and the more complete its separation from the sulphuric acid the smaller is the decomposition, and the smaller is the darkening of the residue left after distillation. The residue left in the flask after the distillation is weighed.

Corrections necessary for losses due to adherence of the fraction to the walls of the container, and to evaporation while transferring from the funnel to the beaker and to the flask are determined experimentally, check experiments being made for this purpose (without distillation) with fractions of corresponding boiling points. The experiments in question required a correction of about 1.5 grams. As has been stated above, the total amount of aromatics and unsaturates equals the loss after the treatment with sulphuric acid and the residue after redistillation.

Since aromatic hydrocarbons are practically absent in the fraction boiling below 60°C., the total of aromatics and unsaturates found in

this fraction is accepted as the amount of unsaturates, this being the only determination of unsaturates made for this fraction.

In the remaining fractions the aromatics are determined as follows: forty grams of the fraction under test is charged into a long neck 200-cc. round bottom flask. The weight is determined within 0.1 gram. The flask is then closed with a rubber stopper provided with a thermometer (the bulb is immersed in the liquid) and a glass tube or a small funnel for the admission of bromine.

The flask containing the fraction is placed in a cooling medium of snow and salt. As soon as the temperature of the fraction reaches -20°C . bromine is added drop-wise from a burette, the liquid being continuously agitated, and attention is paid to the temperature, which should not exceed -18°C . The theoretical amount of bromine required for the saturation of the unsaturates is calculated by the iodine number.

The bromination is finished when the contents of the flask acquire a bright orange color which does not disappear because of the excess of bromine. This is observed, as a rule, when a few per cent in excess of the theoretically required amount of bromine has been added. The flask containing the reaction mixture is kept in the cooling medium for another minute. Then 20 cc. of a 10-per cent solution of caustic soda is added for the neutralization of the excess bromine. The mixture is agitated and transferred to a separating funnel. The caustic is discharged and the remaining product is washed with water until a neutral reaction is obtained. To obtain a separation of the saturated part of the fraction from the dibromides the product is vacuum distilled. The end of the distillation is indicated by a sharp rise in temperature. The condenser and the receiver must be cooled. This is particularly true for the $60-95^{\circ}\text{C}$. fraction. The temperature should be kept at about -60°C . (solid carbonic acid and alcohol).

Because a part of the dibromides is carried over into the distillate in vacuum distillation, the distillate is redistilled. Two distillations with a dephlegmator are carried out, as a rule, under normal pressure, the second distillation being carried out preferably over metallic sodium.

The original fraction is freed from unsaturates by this method. The determination of aromatic hydrocarbons is then made by the usual aniline method. The aniline point determination of the fraction follows bromination and redistillation. To remove the aromatic hydrocarbons, the fractions are shaken energetically for 15 minutes with two volumes of 98 ± 1 per cent sulphuric acid. This is followed by two more treatments with fresh sulphuric acid, each treatment being continued for 15 minutes, using one volume of sulphuric acid for each of these additional operations. The product obtained is washed with water, then with alkali, then with water again to a neutral reaction and finally it is dried over fused calcium chloride. The critical solubility temperature is then checked again. The increase in the aniline point multiplied by the

coefficient gives the content of aromatics in the fraction freed of unsaturates. The coefficient for aromatic hydrocarbons is as follows:

Fraction Boiling Range (°C.)	Coefficient
60- 95	1.15
95-122	1.20
122-150	1.25
150-200	1.50

The amount of aromatics found must be recalculated to the original fraction, which is accomplished by using the following equation:

$$X = X_1 \frac{100 - S}{100 - X_1}$$

where

X = the amount of aromatics in the original fraction in per cent by weight;

X_1 = the amount of aromatics found after the removal of unsaturates;

S = the total of aromatics and unsaturates.

The content of unsaturated hydrocarbons is obtained by the difference between the total content of aromatics and unsaturates and the amount of aromatics. The determination of naphthenes and paraffins is carried out by the method described in the following section.

Hoog and Eichwald^{24b} remove unsaturates selectively with the aid of thioglycolic acid, forming acidic compounds with unsaturates. The reaction takes place at room temperature in propionic acid solution with an excess of thioglycolic acid for 16 hours. The compounds formed can be removed from the hydrocarbons by washing with alcoholic caustic solution. The separation of unsaturates is reported to be complete.

In addition to the above methods involving the selective removal of unsaturates, it should be remembered that the unsaturates can be hydrogenated selectively at moderate temperatures and pressures in the presence of such catalysts as nickel (page 196). In the last method the unsaturates are not separated from other hydrocarbons, but are transformed into saturated hydrocarbons. This method may give very reliable results on the content of unsaturates and aromatics, which are determined after hydrogenation by reaction with sulphuric acid.

Grosse and Wackher^{22a} determine the percentage of aromatic hydrocarbons by means of the specific dispersion (the difference in the indices of refraction for $H\alpha$ and $H\beta$ divided by the density). The specific dispersion, δ , multiplied by the factor 10,000, is 99 ± 1 for all paraffins and naphthenes boiling in the range of gasolines. It is appreciably higher for monoölefins (about 115) and very high for aromatics (from 171 to 190). Diolefins have a very high value of dispersion and are removed with maleic anhydride, if present in an appreciable amount. The percentage of olefins is determined, for instance, by the method of bromine number, and the increment of dispersion due to olefins is accepted as

equal to 0.16 times bromine number. The percentage of aromatics is calculated by the formula

$$\frac{\delta_{fr} - 0.16 \times \text{bromine no.} - 99}{\delta_{\text{arom}} - 99} \times 100$$

The values of δ_{arom} vary from 190.2 for the benzene fraction (70-95°C.) to 171.0 for the fraction 175-200°C., and δ_{fr} is determined experimentally for each fraction. The accuracy of the method depends on the accuracy of determination of the olefins.

Determination of Naphthenes and Paraffins

Cracked gasolines or their narrow fractions, after treatment with three volumes of sulphuric acid and redistillation, consist of naphthenes and

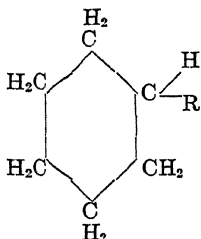
Table 132. Determination of the Content of Naphthene Hydrocarbons by the Aniline Point Method.

Aniline Point (°C.)	Content in Naphthenes by Weight			150-200°C. Fraction
	60-95°C. Fraction	95-122°C. Fraction	122-150°C. Fraction	
76				0
75				5
74				10
73			0	15
72			4	20
71	0	0	9	25
70	3	4	13	30
69	6	8	18	35
68	9	12	22	40
67	12	16	26	45
66	15	19	31	50
65	18	23	35	55
64	21	27	40	60
63	24	31	44	65
62	27	34	48	70
61	30	38	52	75
60	33	42	56	80
59	36	45	60	85
58	39	49	65	90
57	42	53	69	95
56	44	56	73	100
55	47	60	77	
54	50	63	81	
53	52	67	85	
52	55	70	88	
51	58	74	92	
50	61	77	96	
49	64	81	100	
48	67	84		
47	70	87		
46	73	90		
45	75	93		
44	77	97		
43	80	100		
42	82			
41	85			
40	87			
39	90			
38	92			
37	95			
36	98			
35	100			

paraffins. The percentages of these hydrocarbons may be calculated on the aniline points of the naphthene-paraffin fractions. The calculation of the percentage is made by using Table 132. The total amount of any given class of hydrocarbons in the original sample is obtained by adding together the respective amounts so determined of the given class in the individual fractions.

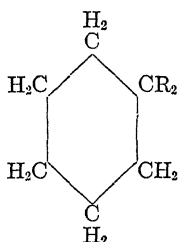
The percentage of naphthenes includes the derivatives of cyclopentane and cyclohexane. Other types of naphthenes may be present in cracked gasolines only in insignificant amounts. The partial percentage of cyclohexanes can be determined by the method of Zelinsky discussed in Chapter 1. The fraction, after the removal of unsaturates and aromatics, is catalytically dehydrogenated in the presence of palladized or platinized asbestos or charcoal at 300°C. The reaction is performed in a tube filled with the catalyst. The rate of the feed is very slow, a few drops per minute. The process is usually repeated two or three times up to complete dehydrogenation of the cyclohexanes. The difference in the aniline points before and after dehydrogenation, multiplied by the aniline factor for the given fraction, gives the percentage of cyclohexanes dehydrogenated. The calculated percentage of cyclohexanes may be recalculated on the original gasoline, as has been shown for aromatics and olefins.

The percentage of paraffins calculated by the aniline method includes normal and iso-paraffins which have about the same aniline points at equal molecular weights. The separate determination of iso-paraffins would have great practical interest in view of the high octane numbers of iso-paraffins. There are no reliable methods for the determination of iso-paraffins so far. Schaarschmidt⁴⁶ showed that antimony pentachloride may be used for the separation of iso-paraffins of tertiary structure from normal and quarternary paraffins. The alkylated naphthenes of the formula



have the same tertiary structure of the alkylated carbon-atom and react with antimony pentachloride as tertiary iso-paraffins. Thus the reaction with antimony pentachloride may determine only the total amount of tertiary iso-paraffins and tertiary alkyl naphthenes. A very approximate evaluation of the percentage of iso-paraffins may be obtained by subtracting the percentage of naphthenes from the total percentage of iso-

paraffins and alkyl naphthenes determined by Schaarschmidt's method. The assumption involved in this calculation, that the naphthenes of cracked gasolines are mostly tertiary alkyl derivatives, might be to a certain degree true. It is likely that the relative amount of non-alkylated cyclopentane and cyclohexane as well as dialkyl derivatives of the general formula



is comparatively small. On the other hand, it should be kept in mind that the iso-paraffins of quaternary structure are not attacked by antimony chloride and cannot be evaluated by this method.

A modification of the Schaarschmidt method has been described by Moldavsky *et al.*³² The reaction with antimony pentachloride is performed after removal of unsaturated and aromatic hydrocarbons because they are easily chlorinated by antimony pentachloride. A weighed amount of antimony pentachloride is used for the reaction. If the temperature of the reaction is sufficiently low—about 0°C. or lower—only iso-paraffins and alkyl naphthenes of tertiary structure are involved in the reaction of chlorination by antimony pentachloride. After standing, white or slightly yellowish crystalline compounds containing 2 molecules of antimony pentachloride per 1 molecule of hydrocarbon precipitate on the walls and bottom of the flask. After the reaction is completed, the reaction mixture is decomposed with water-alcohol mixture containing hydrochloric acid. The amount of antimony pentachloride left after the reaction is determined by titration, and the amount of antimony pentachloride consumed in the chlorination is calculated by difference.

Von Weber⁶⁰ calculates approximately the branching grade Z of a narrow paraffin fraction containing a normal paraffin and its isomers by the following equation:

$$Z = T_0 - T$$

where T_0 is the boiling temperature of the normal paraffin and T the boiling temperature of the fraction. It has been accepted that branching decreases the boiling point of the normal paraffin per 7°C. for each branch. The approximate evaluation of the branching can be carried out only for purely paraffin fractions, for instance, those produced from low-temperature alkylated products. Von Weber determined by this method

the grade of branching in various fractions of hydrogenated kogasin (synthetic gasoline produced by the Fischer-Tropsch method) to be from 0.15 to 0.40. Thus the paraffins in question consist mostly of normal and partially mono-branched hydrocarbons.

Chemical Composition of Commercial Cracked Gasolines

The data on the chemical composition of cracked gasolines, summarized in Tables 133 and 134, were obtained by the methods of Faragher *et al.*,¹⁸ Tilicheyev and Massine,⁴⁴ and Garner.²³ The data on olefins, obtained by the treatment with 80-90 per cent sulphuric acid, are too small and the data on aromatics, obtained by successive treatment with strong sulphuric acid, are too high as compared with the actual content of these hydrocarbons, as has been stated above. The data obtained by this method are not reliable and are not included in the tables. The distribution of various hydrocarbons in the fractions of cracked gasolines is illustrated by the data of Table 133.

Table 133. Fractional Distribution of Hydrocarbons in Cracked Gasolines.

Fraction (°C.)	Percentage by Weight			Paraffins
	Aromatics	Unsaturates	Naphthenes	
Cracked Gasoline from Smackover Crude (Mixed-phase Process)				
0- 45		24		
45- 64		33.3		
64- 95	3.5	43.2		
95-125	7.9	35.7		
125-150	16.1	29.9		
150-180	21.4	29.8		
Cracked Gasoline from Grozny Paraffinic Gas Oil (Mixed-phase Process)				
Below 60	0	53	0	47
60- 95	1	33	14	52
95-122	5	29	18	48
122-150	8	29	16	47
150-200	12	25	22	41
Cracked Gasoline from Surachany Paraffin-base Fuel (Mixed-phase Process)				
Below 60	0	45	0	55
60- 95	1	36	10	53
95-122	1	40	16	43
122-150	5	37	18	40
150-200	8	37	17	38
Hydrogenation Gasoline from Paraffinic Gas Oil (Moderate-temperature Process)				
Below 60	0	10	0	90
60- 95	6.1	8.9	22.9	62.1
95-122	3.0	11.3	29.1	56.6
122-150	5.5	11.3	29.1	54.1
150-200	10.3	9.3	29.1	56.3

The content of olefins as well as paraffins decreases with increasing boiling range of the fraction. The low content of olefins in the first two low-boiling fractions of Smackover-cracked gasoline seems to be rather

exceptional. According to Snow [U.S.P. 2,128,971 (1938)], the composition of the C₅ cracked fraction is as follows:

Pentanes (norm. and iso)	53%
Pentene-1	11%
Pentene-2	20%
Tertiary pentenes	16%

Thus the content of olefins in low-boiling cracked fractions up to 60°C. may be accepted of about 50 per cent. The content of aromatics increases with increasing number of the fraction, as is also observed for straight-run gasolines. The small content of naphthenes varies within comparatively narrow limits.

The chemical composition of various cracked gasolines is given in Table 134. These data show that the chemical composition of cracked

Table 134. Chemical Composition of Synthetic Gasolines.

Origin	Per Cent by Weight			
	Aromatics	Unsaturates	Naphthenes	Paraffins
Mixed-phase (Pressure) Cracking				
1 W. Texas topped crude	13.1	30.8		
2 Panhandle gas oil	10.5	32.8		
3 Seminole fuel oil	9.0	29.1		
4 Smackover crude	16.0	29.1		
5 Panuco crude	15.6	27.3		
6 Pennsylvania crude	7.1	34.6		
7 Grozny paraffin-base gas oil	7.	31	16	45
8 Surachany paraffin-base fuel oil	4	39	13	44
9 Oklahoma City gas oil	10	39	16	35
10 Light gas oil of mixed-base crude	8.5	30	15	46.5
11 Heavy gas oil of same crude	6.5	41	9	43.5
12 Residium of same crude	6	45	8	41
13 Naphthenic kerosene	9	24	35	32
14 Naphthenic residuum	6.5	36.5	11.5	46
Catalytic (Houdry) Cracking*				
Gas oil	15	18	23	44
Vapor-phase Cracking				
16 Mixed gas oil (DeFlorez)	16	49	25	10
17 Gas oil (Gyro)	23	45	14	19
Hydrogenation (Moderate-temperature)				
18 Paraffin gas oil	5	10	22	63
Synthetic processes				
19 Selective polymerization and hydrogen.				100
20 Low-temperature alkylation				100

* Low rate of charge per volume of catalyst per hour.

gasolines, produced in the mixed-phase process, depends upon the nature of the charging stock. The naphthenic and asphaltic crudes (Smackover, Panuco) yield cracked gasolines with a higher content of naphthenes and aromatics. The content of olefins varies in a comparatively narrow range from 30 to 40 per cent. The content of naphthenes is small even in the gasolines from naphthenic stocks, especially as compared with straight-run gasolines.

Catalytic (Houdry) gasolines, produced at low space rates of charge

per volume of catalyst per hour, are less unsaturated and more aromatic than gasolines obtained in pressure cracking, as has been discussed in detail on page 151. The heavy naphtha fraction of thermally cracked gasolines contains from 10 to 20 per cent aromatics and about 30 per cent unsaturates. According to Holaday,^{34c} Houdry cracked naphtha (sp.gr. 0.85, b.r. 330-397°F.) is also more aromatic and less unsaturated:

olefins	4%
aromatics	36%
naphthenes & paraffins	60%

Vapor-phase-cracked gasolines have a higher percentage of olefins and aromatics. The percentage of aromatics is not necessarily great in vapor-phase-cracked gasolines, unless the temperature of the process is very high, about 700°C. (1292°F.).

Hydrogenation gasolines produced at moderate temperatures have a small percentage of aromatics in contradistinction to the highly aromatic gasolines produced in high-temperature destructive hydrogenation. Hydrogenation gasolines have usually a lower content of unsaturates than that given in Table 134, not exceeding 1-2 per cent.

The production of predominantly aromatic gasolines, containing 50 per cent and more of pure aromatics, at very high cracking temperatures of 700°C. (1292°F.) to 800°C. (1472°F.) has been mentioned in Chapter 2, (page 165).

Gasolines formed by the catalytic polymerization of gases (U.O.P. Process) contain a high percentage of unsaturates, above 50 per cent. The catalytically polymerized gasolines consist of olefins, naphthenes, paraffins, and aromatics.

The gasolines resulting from high-pressure thermal conversion of gases are less unsaturated. The content of unsaturates does not exceed 35 per cent, the percentage of paraffins and naphthenes being high.

The knowledge of the individual hydrocarbons present in cracked gasolines is very meager. Of the aromatic hydrocarbons, benzene occurs in a very insignificant proportion. As the data of Table 133 clearly show, toluene and particularly high-boiling alkyl derivatives of benzene are predominant.

The unsaturated hydrocarbons of cracked gasolines are mostly olefins. According to Tongberg, Nickels, Lawrosky and Fenske,⁵³ 6-, 7-, and 8-carbon-atom olefins predominate in a Pennsylvania Dubbs cracked gasoline. According to Brame and Hunter,⁵ cyclic olefins occur mostly in the middle boiling range from 90°C. (194°F.) to 120°C. (248°F.). Diolefins are present in the low-boiling fractions of cracked gasolines. The percentage of diolefins in mixed-phase cracked gasolines does not exceed 0.1 per cent of the total gasoline, and is much higher in vapor-phase-cracked gasolines, amounting to 1 per cent or more. Birch and Scott¹ removed the diolefins in a vapor-phase-cracked gasoline by reaction with maleic anhydride. Butadiene, piperylene, isoprene and cyclopentadiene

were easily separated and were identified in the low-boiling fractions corresponding to the boiling temperatures of these hydrocarbons.

Birch and Hague^{1a} investigated the composition of benzol produced from Persian natural gas at 850°C. The content of pure benzene was close to 75 per cent. In addition to butadiene and cyclopentadiene, the benzol contained approximately 5 per cent styrene and 2 per cent indene. These hydrocarbons, being formed at high temperatures, may occur in small amounts in vapor-phase-cracked gasolines.

The formation of diolefins in cracking may be considerable under certain conditions. Tropsch *et al.*^{53a} cracked a Pennsylvania gas oil at 950°C. and 175 mm. pressure for 0.05 second and produced 6.6 per cent butadiene, 3.1 per cent pentadiene and 7.2 per cent higher conjugated dienes with reference to the oil decomposed.

The naphthenes of cracked gasolines are either the derivatives of cyclopentane or those of cyclohexane. The presence of other naphthenes has not been proved.

Unfortunately, the paraffins of cracked gasolines belong mainly to normal paraffins or slightly branched iso-paraffins. It should be emphasized that the slightly branched C₈ and higher paraffins have moderate octane numbers. For instance, the octane number of octanes with one branch is about 50 or lower. The octane number of nonanes and decanes with one branch is about 30 or lower. Thus only the presence of highly branched paraffins (with at least two branches in C₇ and C₈ and with three branches in C₉ and higher paraffins) brings about a high octane rating of paraffinic gasolines. The cracking gasolines containing a considerable percentage of paraffins, produced from Pennsylvania or Mid-continent crudes, have low octane numbers, corresponding to the normal or slightly branched structure. Octane numbers of paraffinic hydrogenated gasolines also are low. The predominance of straight-chain or slightly branched paraffins should be expected, taking into consideration that the high temperature of cracking favors the formation of more stable normal paraffins (Eq. 2). Brame and Hunter,⁵ however, isolated some iso-paraffins from a Cross cracked gasoline. The catalytic Houdry gasolines probably contain a large proportion of iso-paraffins due to the alkylation reactions in the presence of a catalyst, as has been discussed above (p. 151). Peterkin *et al.*^{36a} give such high figures for the content of iso-paraffins in Houdry gasolines as 63 per cent in a gasoline from paraffinic charging stock, and 47 per cent in another gasoline from naphthenic charging stock. The method of determining iso-paraffins, however, was not disclosed in the article.

In addition to various hydrocarbons, the cracked gasolines contain a small amount of sulphur, oxygen and nitrogen compounds. The sulphur compounds are pre-formed in cracked gasolines, while the oxygen compounds can be yielded by the oxidation of unstable hydrocarbons with air. The formation of these oxygenated compounds and their influence

on the properties of cracked gasolines will be discussed in a special section.

In addition to the oxygen compounds formed by oxidation with air, there is a small amount of other oxygen derivatives which are present in freshly produced cracked gasolines. These pre-formed oxygen compounds belong mostly to phenols and occur in high-boiling fractions of cracked gasolines. The cracked gasolines produced from naphthenic and asphaltic crudes contain a larger proportion of phenols than do paraffinic cracked gasolines. The phenols are washed from cracked gasolines by treatment with caustic soda solution, forming phenolates, and are recovered from the spent caustic. The content of phenols of about 0.1 per cent of the total gasoline is not uncommon for some Gulf and California cracked gasolines, but the average percentage of phenols in cracked gasolines does not exceed 0.01 per cent.

Story and Snow⁵¹ studied the phenols extracted from cracked gasolines and found that they consist of various high-boiling derivatives of phenol, such as cresols, with very little or no carboic acid. Cresols, xlenols, etc., were isolated from Japanese and Persian cracked distillates. Potts and Morrow^{38a} detected trimethylhydroquinone in a cracked distillate from a Texas crude.

The nitrogen compounds occur in cracked gasolines in minute amounts mostly in the form of the derivatives of pyridine and other nitrogen organic bases. The nitrogen compounds are washed with dilute solutions of inorganic acids, forming salts, and are recovered from the acid solution. Bratton and Bailey^{5a} isolated from a California cracked gasoline methyl-, dimethyl-, and trimethylpyridines, quinoline and quinaldine. In contrast to straight-run distillates, only aromatic nitrogen bases were encountered in the cracked gasoline. The nitrogen compounds are present mainly in cracked gasolines from naphthenic and asphaltic crudes.

The sulphur derivatives of cracked gasolines are discussed in a separate section of this chapter.

The determination of the chemical composition of gasolines and particularly of cracked gasolines is a rather laborious operation. For this reason, the data on the chemical composition of cracked gasolines are scarce and frequently unreliable. Unfortunately, there is no direct correlation between the chemical composition of gasolines and such properties as aniline point, iodine number, acid heat, etc. Nevertheless, these constants may be of value for an approximate evaluation of the chemical composition of cracked gasolines.

The aniline points or critical temperatures of solubility of cracked gasolines in aniline denote to a certain degree the chemical composition of gasolines. High aniline points are characteristic of those containing a large proportion of paraffins. Normal and iso-paraffins of the same molecular weight have about the same aniline points, around 71-76°C. for the hydrocarbons boiling in the range of gasolines. Naphthenes boiling in the same temperature range have lower aniline points, from 35 to

56°C., increasing with the boiling point of naphthenes. Olefins and other unsaturates have still lower values of aniline points, from 10 to 45°C. The aniline points of aromatic hydrocarbons boiling in the range of gasolines are very low, less than -30°C.

The aniline points of commercial cracked gasolines vary from 10°C. for vapor-phase-cracked gasolines to 40°C. for gasolines cracked in the mixed phase. Moderate-temperature hydrogenation produces gasolines having aniline points of 40°C. and higher. The highly aromatic hydrogenation gasolines of high-temperature processes have values of aniline points of -10°C. and lower.

The aniline points are determined by the following procedure. Five cc. of cracked gasoline and five cc. of freshly distilled aniline are placed in a test-tube (25 mm. in diameter and 150 mm. long) provided with a glass stirrer, or a solid wire, as well as with a thermometer. The test-tube is fixed in a wider tube which acts as an air jacket and is heated in a glass of water. The aniline point is the temperature at which aniline and gasoline are completely miscible. The point is determined as the temperature of complete miscibility of two phases, or as the temperature of separation of two phases from the homogeneous mixture. The first determination is made on heating two layers of aniline and gasoline; the second is made on cooling the homogeneous mixture of aniline and gasoline obtained above the critical temperature.

It should be pointed out that the values for specific gravities or refractive indices of cracked gasolines may be of the same value for the provisional chemical characteristics as those of aniline points.

As has been stated above, bromine or iodine numbers are very significant for the evaluation of unsaturated hydrocarbons in cracked gasolines. The iodine numbers may be as high as 150-250 for vapor-phase-cracked gasolines. They vary from 50 to 120 for mixed-phase-cracked gasolines.

The acid heats, like iodine numbers, are an approximate measure of the content of unsaturated hydrocarbons in cracked gasolines. The test is performed with 150 cc. of the tested gasoline and 30 cc. of concentrated sulphuric acid in a Thermos bottle with vigorous shaking. The increase in temperature is the acid heat of the gasoline tested. Unsaturation is largely responsible for the heat evolved in the reaction with sulphuric acid. Aromatic hydrocarbons react more slowly, with a comparatively mild increase in temperature. The values of acid heat for cracked gasolines vary from 200°F. or more to 20-30°F., the last figure being obtained for vapor-phase-cracked gasolines and the last ones for mixed-phase-cracked gasolines treated with sulphuric acid. Mixed-phase-cracked gasolines, untreated or clay treated, have an acid heat of about 100°F. The maximum value of acid heat allowed by some commercial specifications of aviation gasolines is from 15 to 20°F. These values correspond approximately to the content of olefins, from 7 to 10 per cent by weight.

The iodine numbers and acid heat of hydrogenation gasolines are very low.

The data on the specific gravities, aniline points, iodine numbers and acid heats of various cracked gasolines E.P. 400°F. are summarized in Table 135.

Table 135. Average Specific Gravities, Aniline Points, Iodine Numbers and Acid Heats of Cracked Gasolines (Untreated).

Cracked Gasoline	Specific Gravity at 15°C.	Aniline Point (°C.)	Iodine Number	Acid Heat (°F.)
Mixed-phase, from Pa. or M.C. crude	0.730	40	100	120
Mixed-phase, from naphthenic crude	0.750	30	100	120
Vapor-phase	0.770	10	200	200
Hydrogenation, moderate-temperature	0.720	50	5	5
Hydrogenation, high-temperature	0.800	-10	5	5
Catalytic, Houdry	0.730	30	50-100	60-120
Catalytic polymerization of gases	0.735	30	150	
Thermal conversion of gases	0.720	40	100	

Oxidation and Gum Formation

Oxidation of unstable hydrocarbons of cracked gasolines produces certain oxygen compounds which are soluble primarily in gasolines. The formation of these compounds progresses when an unstable cracked gasoline exposed to air is stored for a prolonged time. The condensation of the oxygen compounds soluble in gasoline leads to the formation of gums which are insoluble in hydrocarbons and are deposited as gummy liquids.

When a sample of a cracked gasoline containing oxygenated compounds is evaporated in the absence of air, it leaves a certain amount of gum insoluble in gasoline. Thus the transformation of soluble oxidation compounds, or "soluble" or "dissolved" or "pre-formed" gum, into insoluble gum may be performed without further oxidation.

When a cracked gasoline is used in engines as motor fuel, the gum can be deposited in the fuel-feed tubing, carburetor and other parts of the engine. On the other hand, carbon can be deposited in the combustion spaces, as a result of the decomposition of unstable gum at high temperatures of combustion.

The content of dissolved gum in cracked gasolines predetermines the actual gum-forming properties of gasolines in engines. Gum formation is a rather slow chemical process, and the time of use of gasoline in an engine is too short to allow an appreciable amount of gum to form. The content of dissolved gum, however, changes with time of storage, depending on the nature of gasoline and the conditions of storage. The formation of dissolved gum in a cracked gasoline *versus* time may be illustrated by the data of Scheumann⁴⁷ presented in Table 136. Thus the cracked gasoline in question, satisfactory with respect to the content of dissolved gum within 2-3 months of storage, was quite deteriorated after 6 months of storage. The formation of gum is the simple logarithmic function of the time. Thus Yabroff and Walters⁵⁶ showed that the X-mgr. gum time

Table 136. Gum Formation in Storage.

Time of Storage (days)	Dissolved Gum (mg. per 100 cc.)	Rate of Gum Formation per 2 months
0	0	
60	1	1
120	3	2
180	26	23
240	64	38
300	101	37

(or the time required for formation of X mgr.) may be computed from the initial gum content of the gasoline I and the 10-mgr. gum time:

$$X\text{-mgr. gum time} = 10\text{-mgr. gum time} \times \frac{\log X - \log I}{\log 10 - \log I}$$

The kinetics of the formation of dissolved gum show a very important phenomenon of induction. As Table 136 shows, the formation of gum may take place very slowly during first months of storage. Then the rate of formation may suddenly increase, and oxidation will continue with high rate of the process. The period during which the rate of the process is nil or very slow is the so-called induction period.

Yabroff and Walters⁵⁶ apply equations 32 and 33 to gum formation. They calculated the activation energy of this reaction to be about 27,000 Cal.

The formation of gum in storage depends on the content of unstable gum-forming hydrocarbons which are gradually oxidized and which are specified as the "potential" gum of cracked gasolines. The conception of the potential gum, however, is fairly indefinite, in contradistinction to the dissolved gum. There is no sharp distinction between hydrocarbons stable and unstable with respect to oxidation. On the other hand, the extent of oxidation depends on the conditions of oxidation. The determination of the potential gum may be conventional only under arbitrarily specified conditions of oxidation. The amount of potential gum should predetermine the stability of cracked gasolines in storage.

Gum formation as a result of polymerization of diolefins present in cracked gasolines does not take place to any appreciable extent without oxidation. The concentration of diolefins, even in vapor-phase-cracked gasolines, is evidently too small to bring about polymerization and gum formation. Thus the presence of oxygen or air is a necessary prerequisite for gum formation.

Dissolved Gum

The content of dissolved gum is determined by rapid evaporation of cracked gasolines under such conditions that no further oxidation and gum formation occurs. The rapid evaporation of cracked gasolines in a steam-jet seems to be an operation completely conforming to the above-mentioned conditions. This method can be used for determining the dissolved gum. Hunn, Fischer and Blackwood²⁵ showed that the steam-

jet may be replaced by the air-jet in this operation without any oxidizing action, provided the time of operation is short. The tests are made in porcelain or glass dishes. The use of metallic dishes is avoided due to the catalytic action of many metals on the oxidation of hydrocarbons.

The procedure is carried out as follows. A 50-cc. sample of a cracked gasoline in a Pyrex brand dish (9 cm. in diameter) is evaporated on a steam bath. An air-jet is placed vertically over the dish at a distance of 4 cm. from the initial surface of the sample. The hole in the air-jet is 1/16 inch and the air pressure is maintained at the equivalent of 2 cm. of water. The dish with the sample remains on the steam bath 1 hour or more. The final drying is performed in an oven at 150°C.

In another widely used modification of this method, an ethylene glycol bath is used instead of a steam bath, at a higher temperature of about 320°F. The time of evaporation is shortened to 8-14 minutes. The figures produced by this modification are close to those of the first modification on the steam bath, being usually a little smaller.

Dissolved gum is formed as a result of oxidation, as has been pointed out above. Thus, freshly distilled cracked gasolines are entirely free of dissolved gum.

There is a rough correlation between the content of dissolved gum in cracked gasolines and gum formation in engines. Voorhees and Eisinger⁵⁴ and Hunn, Fischer and Blackwood²⁵ showed that gasolines containing 10 mg./100 cc. or less of dissolved gum by the air-jet method give very satisfactory operation without deposit of the gum in engines. This content of dissolved gum may be considered as a guarantee of satisfactory gum-forming properties of gasolines in engines at the time of test. It should be emphasized, however, that the deposition of gum in engines depends on many other factors not connected with the properties of the gasoline used, such as manifold temperature, etc. The content of potential gum has no influence on gum formation in engines. The dissolved gum only is responsible for the gum-forming properties of gasolines in engines.

The content of dissolved gum is not connected directly with the storage stability of cracked gasolines, as has been mentioned above. For instance, a cracked gasoline with 0-2 mg. of dissolved gum may be stable or unstable in storage depending upon the proportion of oxidizable compounds or potential gum. A considerable content of dissolved gum, however, indicates that the gasoline might be unstable in storage. According to Yabroff and Walters,⁵⁵ from 25 to 100 mg. of dissolved gum are formed in gasoline when the end of the induction period is reached and the gasoline breaks down.

Potential Gum and Stability of Cracked Gasolines

The content of potential gum can be determined by the oxidation of a sample of gasoline under specified conditions. According to Voorhees and Eisinger,⁵⁴ the procedure is as follows: a 25-cc. sample of a cracked

gasoline in a 500-cc. flask filled with oxygen is heated in a steam bath for 5 hours. After heating, the apparatus is cooled, the oxidized sample is transferred to a porcelain glass dish and evaporated in a steam oven. Stable cracked gasolines that can be stored for at least a year without excessive gum formation give 8-40 mg./100 cc. of potential gum by this test, while unstable gasolines may form 1000 mg. or more. Frequently the figures of potential gum produced by this method are comparatively close to those obtained in the copper-dish determination.

Another widely used method of accelerated oxidation determining the stability of cracked gasolines is performed at 100°C. in a bomb under 100 lbs. initial cold oxygen pressure.

A recording pressure gauge attached to the bomb indicates the rate of absorption of oxygen by the gasoline. The oxidation of gasoline in the bomb, as well as in storage, takes place very slowly in the first stages of oxidation, indicating the induction period, after which the gasoline is rapidly oxidized. As a result, the gasoline "breaks down" and the pressure suddenly drops after the induction period is over. The induction period is taken as a measure of the stability or of the gum-forming properties of gasolines in storage.

A modification of this method is used for testing aviation fuels. A 200-cc. sample of gasoline is oxidized for 5 hours at 212°F. under 100 lbs./sq. in. initial cold oxygen pressure in the presence of iron catalyst consisting of 35 square inches of iron tubing. The quantity of gum formed is determined by evaporation in a Pyrex brand dish. It should not exceed 6-10 mg. per 100 cc. according to U. S. Army specifications.

According to Rogers, Bussies and Ward,⁴¹ there is a close connection between the induction periods and the storage life of cracked gasolines. For instance, the time required to form 10 mg./100 cc. of dissolved gum at a given temperature depends greatly on the induction period. The 10-mgr. gum time (or the time required to form a gum content 10 mgr./100 cc.) is from 30 to 75 per cent of the induction period for various gasolines.⁵⁶ Winning and Thomas,⁵⁵ however, did not find a simple correlation between the stability in storage and the induction period of cracked gasolines. They recommend the use of the induction period test in conjunction with the copper dish test to predict more accurately the storage life of gasoline. Dryer, Morrell, Egloff and Lowry¹³ find that the induction period is the most reliable test in predicting the storage stability. A gasoline which shows an induction period of five hours or more may be considered, with certain reservations, as sufficiently stable for prolonged storage up to a year.

Notwithstanding a sharp criticism of this method the determination of gum formation in a copper dish is widely used. The copper dish method is essentially an oxidation test, but without control of the conditions of oxidation. The procedure lasts for a comparatively long time, from 2 to 3 hours. The copper and copper oxide exercise a strong catalytic action upon the oxidation and formation of gum. The oxidation of vari-

ous fractions takes place under different conditions. The heavy and high-boiling fractions are oxidized more strongly than the low-boiling cuts, which are evaporated in the first stages of the procedure. The copper dish test gives comparatively high figures of gum, usually many times higher than the figures of dissolved gum. It is evident that a direct relationship between the content of dissolved gum and copper dish results cannot be expected.

As has been previously pointed out, the content of copper dish gum may give some estimation of the life and storage stability of cracked gasolines, particularly in conjunction with the induction periods. The cracked gasolines having very low values of copper dish gum, usually are stable in storage. On the other hand, the cracked gasolines with high values of copper dish gum may be either unstable or sufficiently stable in storage. Thus the determination of induction periods is necessary for a better estimation of storage stability. The gum-forming properties of cracked gasolines in engines do not depend upon the copper dish gum test. The gasolines having high figures of copper gum frequently are satisfactory as motor fuels and do not form gum deposits in engines.

The practical specifications of the permissible content of copper dish gum vary from 10 to 40 mg./100 cc. The maximal content 20-25 mg./100 cc. may be used as an average and fairly reliable specification, particularly in conjunction with induction periods of 5 hours or more.

The procedure for determinating gum in a copper dish is as follows: 100 cc. of gasoline in a freshly polished copper dish (3½ inches in diameter) are evaporated on a boiling steam bath until all volatile constituents have disappeared. The final drying is performed in an oven at 110°C. for 30 minutes.

Some data of Morrell *et al.* summarized in Table 137, give an idea of the results produced by the methods of determining gum formation discussed above.

Table 137.

Cracked Gasoline	Dissolved Gum Air-jet Method (mg./100 cc.)	Copper Dish Gum (mg./100 cc.)	Induction Period (minutes)
Treated Midcontinent	2	94	255
Untreated Pennsylvania	0	31	65
Treated Pennsylvania	0	8	120
Untreated California	26	495	445
Treated California	0	16	1600+

There is no correlation between the figures of the copper dish gum and those of the induction period for the gasolines of Table 137. The difference between the air-jet method, giving dissolved gum, and two other methods, giving potential gum, should be kept in mind.

Factors of Gum Formation

As has been stated above, the rate of gum formation has an induction period depending on the nature of the cracked gasoline, *i.e.*, on the content

of unstable gum-forming hydrocarbons. The rate of gum formation greatly increases when the content of dissolved gum becomes comparatively high. The gum formed acts as a catalyst and induces further oxidation and gum formation. Thus an appreciable content of dissolved gum is an indication that the stability of the gasoline in storage is questionable.

Acids may also be catalysts of gum formation. In many cases the rerunning of pressure distillates after treatment with sulphuric acid and caustic is accompanied by the formation of small quantities of sulphur dioxide due to the decomposition of dialkyl esters of sulphuric acid. Sulphur dioxide dissolved in redistilled cracked gasoline is a very powerful catalyst of gum formation. The stability of treated gasolines in such cases may be much less than that of raw pressure distillates. Even traces of sulphur dioxide in finished gasolines may impair its stability and color.

In addition to certain oxygen compounds and acids, gum formation is apparently accelerated by some sulphur compounds, particularly by mercaptans and, to a lesser extent, disulphides.^{43a}

Other factors favoring gum formation are the temperature, light and easy access of air. The influence of temperature is very strong. In accelerated gum formation at 100°C., the induction period usually does not exceed several hours, while at room temperature it may last many months. Mardles and Moss²⁹ give the following figures on gum formation at various temperatures (Table 138). Therefore, deterioration of cracked

Table 138. Period of Storage Giving a Dissolved Gum Content of 10 mg./100 cc. for a Mixed-phase-cracked Gasoline.

Temperature (°C.)	Time
15	More than 100 days
35	9 days
50	2 "
75	5.5 hours
90	2.5 "

gasolines is greater at summer temperatures and in tropical countries.

The influence of sunlight upon gum formation is very considerable, but is less significant from the practical standpoint. An easy access of air to cracked gasoline enormously accelerates gum formation. According to Mardles and Moss, the increase in the content of dissolved gum formed after storage is almost a hundred times more for samples conserved in bottles 1/10 full than in full bottles. An easy access of air and frequent changes of the level of cracked gasolines stored in tanks are the favorable conditions for gum formation. From this standpoint, the use of floating roofs is recommended for the storage of cracked gasolines.

The gum formation and stability of cracked gasolines depend largely on the conditions of cracking. The mixed-phase process gives comparatively stable gasolines. The stability of cracked gasolines increases with increasing pressure of the process. The vapor-phase-cracked gasolines

are unstable and gum-forming. On the contrary, stability of hydrogenation gasolines and, to a lesser degree, gasolines of catalytic cracking (Houdry) is excellent. Table 139 summarizes the data on the gum formation of various untreated cracked gasolines.

Table 139. Gum-Forming Properties of Various Untreated Cracked Gasolines.

Process	Copper Dish Gum (mg./100 cc.)	Induction Period (minutes)
Mixed-phase	50- 500	40-200
Vapor-phase	500-1000 and more	
Reforming	50- 500	40-200
Catalytic (Houdry)*	1- 20	240+
Catal. polymerization of gases	10- 150	30-60
Thermal conversion of gases (clay treated)	10	120
Hydrogenation, moderate-temp.	1	1200+
Hydrogenation, high-temp.	5	1200+

* Low throughput of charge per volume of catalyst per hour.

Chemistry of Gum Formation

The gum deposited during storage of cracked gasolines is a heavy viscous liquid; the gum obtained after the evaporation of gasolines in the tests, described above, is usually a brown solid substance. The same solid gum is formed in the intake systems of gasoline engines. Both the liquid and solid gums are insoluble in hydrocarbons and easily soluble in acetone. The content of oxygen in the gum amounts to 15-20 per cent or more. Various organic compounds, including hydrocarbons, peroxides, aldehydes, ketones and acids, can be separated from gum. According to Story, Provine and Bennet,⁵⁰ there is no substantial difference between liquid and solid gums. Acids, soluble and insoluble in water, are the principal constituents of gum. The amount of unsaponifiable matter in the copper dish gum is 13 per cent and that in the liquid gum, formed in sunlight, is 21 per cent, other constituents being saponifiable in alcohol solution.

The hydrocarbons responsible for gum formation in cracked gasolines belong to the class of unsaturated hydrocarbons. It is well known that straight-run gasolines, containing paraffins, naphthenes and aromatics, do not form any gum. Flood, Hladky, and Edgar²⁰ investigated the oxidation of various hydrocarbons at low temperatures, using the conditions of the standard tests. Most of the monoölefins are comparatively stable with respect to gum formation. At high concentrations, however, the oxidation of monoölefins may be noticeable. Cyclic olefins with one double bond are less stable than open-chain olefins. The principal gum-forming hydrocarbons are aliphatic and cyclic diolefins and mono- or diolefins attached to the benzene ring. Of the diolefins, the conjugated hydrocarbons are very readily oxidized, while the hydrocarbons containing widely separated double bonds are much more resistant. The difference in the behavior of various hydrocarbons in oxidation is enormous. For instance, under the same conditions (100°C., 100 lbs. pressure, 10 per cent concentration of the hydrocarbon in standard gasoline, 4 hours),

pentene produced 0 mg. of gum, 1-octene 0 mg., cyclohexene 0 mg., styrene 3034 mg., 2,4-hexadiene 1173 mg., and 1,3-cyclopentadiene 4085 mg.

The gum-forming property of hydrocarbons is closely connected with the formation of peroxides. For instance, Hock and his collaborators^{24a} showed that cyclic olefins form peroxide much more easily than open-chain olefins. Cyclohexene formed 19 per cent peroxides for 200 hours at 30-40°C., while normal hexene under the same conditions gave only 0.4 per cent peroxides. It is of interest that the formation of peroxides increases in the presence of such catalysts as cuprous chloride.

Martin, Gruse and Lowy³⁰ found that the narrow fractions of a vapor-cracked gasoline forming very large amounts of gum corresponded to the boiling ranges: 73.9-79.4°C.; 101.7-107.2°C., and 123.9-129.4°C. The following diolefins boil in the same boiling ranges: methylpentadienes (74-77°C.), cyclohexadienes (78.5-80.5°C.), methylcyclohexadienes (108-110°C.), heptadiene (107°C.), methylhexadiene (107-109°C.), dimethylhexadiene (125-130°C.), methylethylhexadiene (127°C.), dimethylcyclohexadiene (130°C.).

Frequently the gum-forming hydrocarbons are irregularly distributed even in the large fractions of cracked gasolines. The figures of Thomas⁵² may be of interest with respect to the gum-forming properties of different fractions (Table 140).

Table 140. Fractions of Vapor-phase-cracked Gasoline from Persian Crude.

Fraction	Boiling Range	Specific Gravity	Sulphur Content	Gum content Air-jet (mg./100 cc.)	Gum content Potential (mg./100 cc.)
1	18- 30	0.669	0.08%		
2	30- 40	0.678	0.11	4	93
3	40- 60	0.689	0.08	4	124
4	60- 70	0.699	0.05	7	164
5	70- 80	0.718	0.01	10	222
6	80- 90	0.736	0.04	16	220
7	90-100	0.736	0.04	19	257
8	100-110	0.761	0.145	91	278
9	110-120	0.762	0.14	61	286
10	120-130	0.771	0.13	60	291
11	130-140	0.779	0.23	59	216
12	140-150	0.779	0.16	21	140
13	150-160	0.784	0.19	21	87
14	160-170	0.793	0.16	7	23
15	170-180	0.797	0.15	7	10

An uneven distribution of gum and gum-forming constituents in the fractions of cracked gasolines is also found by Cassar¹⁰ and Mardles and Moss.²⁹ The fractions boiling between 100 and 130°C. (212-266°F.) seem to be particularly rich in gum-forming hydrocarbons. The data of Thomas, as well as of Cassar, show that gum formation is not connected with the sulphur compounds present in cracked gasolines.

As has been observed by Brooks,⁸ the first stage of the action of oxygen upon unstable unsaturated hydrocarbons of cracked gasolines is the formation of peroxides. Even commercial refined cracked gasolines give a very marked positive test for peroxides upon exposure to air and

sunlight for 30 minutes. The peroxides can be easily detected in the first weeks and months of the storage period. The peroxides formed catalyze the further oxidation of cracked gasolines. In the presence of water, dissolving peroxides, gum formation is considerably reduced.

On the other hand, Cassar showed that the peroxides added to cracked gasolines actually catalyzed the gum formation. Peroxidized gasolines may be "rejuvenated" or restored in the induction period after the caustic washing, removing peroxides formed.

Morrell, Dryer, Lowry and Egloff³³ oxidized cracked gasolines by oxygen at 100°C. and confirmed that peroxides are the first products of oxidation. When the content of peroxides formed was sufficiently high,

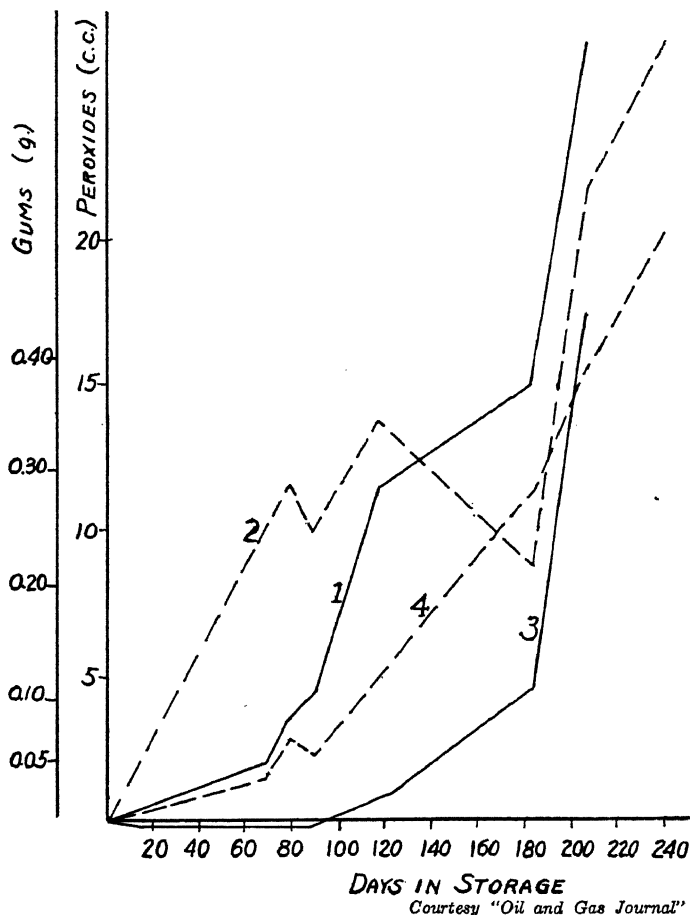
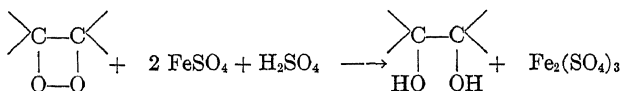


FIGURE 47.—Formation of Gums and Peroxides *versus* Time of Storage. Curves: (1) gums in untreated gasoline; (2) peroxides in untreated gasoline; (3) gums in refined gasoline; (4) peroxides in refined gasoline.

the gum content, both copper dish and air jet, increased to high figures. The same authors showed later¹² that aldehydes and acids soluble in gasoline are formed in the more advanced stages of storage. The relative amount of peroxides, aldehydes and acids soluble in gasoline increases gradually with increasing time of storage. The gum begins to appear as soon as a considerable amount of peroxides has been formed and before any large formation of aldehydes and acids soluble in gasoline. Thus gum formation is closely related to peroxides.

The correlation between peroxides and gum formation may be illustrated by Figure 47 according to the data of Pipik and Mezhebovskaya.³⁸ In general, the increase in peroxides corresponds to the increase in gum content. A decrease in peroxides in certain periods of storage may be explained as a result of the vigorous conversion of peroxides to gum.

Due to the important part played by peroxides in gum formation, estimation of peroxides in cracked gasolines may become a common analytic operation. Yule and Wilson⁵⁷ introduced the peroxide numbers of gasolines as the gram equivalents of active oxygen per 1000 liters of sample. The peroxide numbers are determined by oxidation of ferrous sulphate to ferric sulphate in the presence of peroxides:



The ferric salt formed is titrated immediately with 0.01*N* titanous chloride solution. The details of the operation and corrections are to be found in the original article.

In many cases even such low figures for peroxide number as 2-3 are sufficient for the further rapid gum formation and deterioration of gasolines. Wagner and Hyman⁵⁹ postulated the formation of peracids together with peroxides.

The exact mechanism of the transformation of peroxides into gum is completely obscure. The gum may be formed as a result of the decomposition of peroxides, yielding the high molecular weight acids of gum. On the other hand, the decomposition of peroxides may be accompanied by the condensation of other unsaturated hydrocarbons. The latter hypothesis seems to be the more probable, explaining the part played by more stable olefins in gum formation. Diolefins and other unstable unsaturated hydrocarbons yield peroxides which involve other more stable unsaturates in the further stages of decomposition and condensation. It should be emphasized that the extent of gum formation in the advanced stages of oxidation is much greater than would be expected on the basis of the actual content of diolefins and other unstable unsaturates. Brooks⁸ added the same quantities of unstable unsaturated hydrocarbons (limonene or isoprene) to a straight-run and a refined cracked gasoline and oxidized the mixtures under the same conditions. The formation of gum in the mixtures with cracked gasolines was approximately 10 times

greater than in the case of straight-run gasolines. Thus the oxidation of unstable diolefins involves other more stable unsaturated hydrocarbons of cracked gasolines.

Inhibitors

Oxidation and gum formation in cracked gasolines is a typical chain reaction. In such reactions the addition of small amounts of inhibitors breaks the chain of reactions leading to oxidation and gum formation. The inhibitor is oxidized by peroxides or, more probably, is combined with peroxides, forming some unstable addition compounds. The activation energy of peroxides falls, and they lose their catalytic action and their part in the chain reactions of oxidation. As a result, in the presence of inhibitors the gum-forming properties of cracked gasolines are reduced to an extent depending on the nature and concentration of the inhibitor.

The inhibitors widely used for cracked gasolines are mostly phenols and aromatic amines. Amino-phenols may be very effective as inhibitors. Two isomers, as, for instance, α -naphthol and β -naphthol, may have quite different inhibiting activities. Thus it seems to be impossible to find a closer correlation between the chemical structure and inhibiting activity of organic compounds. Table 141 contains some data on the inhibiting

Table 141. Gum Inhibitors in Cracked Gasoline (Concentration 0.01 Per Cent).

Inhibitor	Induction Period (minutes)
Blank	45
Phenol	75
<i>o</i> -Cresol	135
Thymol	300
Catechol	2400
Hydroquinone	85
Pyrogallol	2185
α -Naphthol	2250
β -Naphthol	330
1,5-Dihydronaphthalene	1705
<i>o</i> -Aminophenol	1320
Aniline	45
<i>p</i> -Phenylenediamine	960
Phenyl- α -naphthylamine	720

properties of various organic compounds investigated by Egloff and his associates.¹⁵

Chlorinated hydrocarbons, alcohols, nitro-compounds, thiophene, and hydrocarbons were completely inactive.

According to Rogers and Voorhees,⁴² methyl-*p*-aminophenol and benzyl-*p*-aminophenol are very powerful inhibitors, more effective than α -naphthol. These inhibitors, being used in a concentration of 0.002 per cent, have a very marked retarding effect, increasing the initial induction period of a gasoline from 200 to 650-1100 minutes. These figures give an idea of the concentrations of inhibitors used commercially. They range from 0.002 to 0.02 per cent depending on the activity of the inhibitor and properties of gasoline.

The following inhibitors are widely used in commercial practice: α -naphthol, benzyl-*p*-aminophenol, dibenzyl-*p*-aminophenol, butyl-*p*-aminophenol, catechol, butylcatechol, some fractions of wood tar, etc.

The retarding effect of an inhibitor is directly proportional to the concentration, at least if comparatively small concentrations are employed.

The inhibiting effect depends not only upon the inhibitor used but also upon the gasoline in which it is used. A choice of an inhibitor for any particular gasoline can be made only as the result of parallel tests of various inhibitors. On the other hand, the inhibitor susceptibility for the same gasoline may be considerably lowered by free sulphur introduced in sweetening or oxygen compounds formed in storage. The doctor sweetening must be carried out with a minimum of free sulphur to avoid the harmful effect of excess sulphur. The influence of oxygen compounds, particularly peroxides, will be discussed later.

The use of various dyes in commercial gasolines is well known. The dyeing of cracked gasolines may be combined with the inhibiting effect by the use of dyes which have an inhibiting action. Lowry, Egloff, Morrell, and Dryer²⁸ name the following commercial dyes which have inhibiting value (Table 142).

Table 142. Dyes—Inhibitors.

Dye	Color Index No.	Color in Gasoline
Oil Brown	73	red
Azo dye, Orange Base	20	yellow
Azine dyes: Induline Base B	860	pink
Nigrosine Base N	864	red-violet
Triphenylmethane dye, Victoria Blue Base B	729	brown-red

When a gasoline containing the inhibitor dye is oxidized in the bomb test, the dye is oxidized and gradually fades during the time it inhibits oxidation. Thus the fading of the gasoline containing an inhibitor dye may be used as an indication of the exhaustion of the inhibitor.

The phenols and cresols present in some cracked gasolines are natural inhibitors. Their removal in the process of treatment may decrease the stability of the treated gasolines. Sager,⁴⁵ for instance, showed that soda washing of a Rumanian cracked gasoline increased the content of potential gum from 320 to 730 mg./100 cc. after treatment with soda solution.

Newton³⁵ repeatedly treated a Trinidad cracked gasoline with a 10-per cent (by volume) solution of sodium hydroxide. The determination of the induction period gave the following results:

No. of Soda Washes	Induction Period (minutes)
0	1320
2	495
4	195
6	210
8	195
10	150
12	120

These data show that the natural inhibitor present in cracked gasoline may have a great effect on the induction period and stability of gasolines. It should be mentioned also that complete removal of the inhibitor is comparatively difficult and requires many operations.

The addition of inhibitors improves the induction period as well as the copper dish test and the content of potential gum. According to Dryer *et al.*, effective inhibition of a gasoline is obtained when the initial induction period increases at least 180 minutes by application of the inhibitor. The amount of the copper dish gum drops many times after inhibition, usually 5-10 times for the small concentrations of inhibitors which are used in commercial practice.

The influence of ageing on the induction period was investigated by Rogers and Voorhees.⁴³ The results are given in Table 143.

Table 143. Effect of Ageing on Response to Inhibitors.

Gasoline	Induction Period (minutes)
Fresh gasoline	130
Same + 0.003% benzene-amino-phenol	460
Fresh gasoline aged 6 weeks	75
Same + 0.003% benzene-amino-phenol aged 6 weeks	250
Same + 0.003% benzene-amino-phenol aged 10 weeks	150

The decrease in the induction period is explained by a gradual oxidation of the inhibitor by the peroxides formed in storage. As has been reported above, the oxidation and fading of inhibitor dyes were actually observed in the accelerated oxidation of gasolines containing an inhibitor dye.

The influence of inhibitors on the storage life of cracked gasolines may be comprehensively illustrated by some data taken from the article of Dryer, Lowry, Morrell and Egloff¹³ (Table 144).

Table 144. Storage Life of Uninhibited and Inhibited Cracked Gasoline.

Gasoline	0	1	2	3	4	5	-Age in Months-				9	10	11	12
Pennsylvania, Untreated, Induction Period 60, Gum	1		7			810	696							
Same + 0.016% Pyrogallol Induction Period 265, Gum	1		0								3			7
Same + 0.00138% Hydroquinone Induction Period 80, Gum	1		0		3	2	31		576	928				
Same + 0.00138% Catechol Induction Period 130, Gum	1		1	6	34	462	424		326	304				
Same + 0.0018% α -Naphthol Induction Period 170, Gum	1		1	2		8	3		5	16	76	418		

Raw and treated cracked gasolines may be inhibited with satisfactory results. Raw cracked gasolines are given a preliminary sweetening with doctor solution. If any other method of treatment is required for a particular cracked gasoline, the degree of the treatment should be much less than for uninhibited gasoline.

The addition of inhibitors to cracked gasolines must be carried out

before any appreciable formation of peroxides. When a gasoline contains an appreciable amount of peroxides, the inhibitor is oxidized by peroxides and the result of the inhibition becomes poor. Thus untreated cracked gasolines are sweetened immediately after production and then inhibited immediately after sweetening. More stable, properly treated, cracked gasolines may be inhibited after a certain time of storage before any significant formation of peroxides has begun. Any excess of sulphur in doctor sweetening is detrimental to inhibition and should be avoided.

In handling and storage of inhibited cracked gasolines, contact with caustic soda solutions should be completely avoided due to the solubility of inhibitors (mostly phenols or phenol derivatives) in caustic solutions, forming phenolates. In addition, certain inhibitors are readily oxidized in the presence of alkali. It should be mentioned also that many inhibitors are fairly soluble in water which can partially extract the inhibitor dissolved in gasoline. Other conditions being equal, the oil-soluble and water-insoluble inhibitors should be preferred to inhibitors of reverse properties.

The rate of the dissolution of inhibitors in cracked gasolines is rather slow. Thus the inhibitors are first dissolved in solvents which are miscible with gasolines, such as ethyl alcohol, acetone, benzene, etc.

According to Nissen and Ross,³⁶ the total cost of inhibiting is from 0.26 to 2.27 cents per barrel treated, including the inhibitor.

Rather and Beard³⁹ found that certain inhibitors, particularly the polyhydroxybenzenes such as hydroquinone, pyrogallol, and diamyl hydroquinone, possess the property of restoring the color of gasolines and kerosenes which have gone off-color in storage. In many cases, the color was restored to very nearly the initial color of the product when freshly refined. The procedure is as follows. One pound of, for example, hydroquinone is dissolved in 1 gallon of a solvent, such as isopropyl or ethyl alcohol, and from 2,000 to 15,000 gallons of the product are treated with one gallon of the solution, with good agitation. Vigorous shaking with water causes the color to return to the product, and it is believed that some loose addition compounds are formed as a result of the treatment described. It is recommended to store the products treated in the absence of water.

Downing, Clarkson and Pedersen¹¹ pointed out that gum formation is strongly promoted by metals and metallic salts. Copper is especially active. The induction period of a cracked gasoline of 110 minutes fell to 30 minutes after contamination with 1 part of copper per 1 million parts of gasoline. The use of inhibitors in such contaminated gasolines gave very poor results. Iron and vanadium have the same effect as copper but to a lesser extent. Some deactivators poison the metallic catalysts in gasolines and suppress their catalytic action. For instance, disalicylal-ethylenediamine in a concentration of 0.001 per cent suppresses the catalytic action of copper. On the other hand, the deactivator by itself does not affect the induction period and stability of gasolines. Tests

made on about 60 samples of commercial gasolines showed that the inhibitor response of many of them was improved by the addition of a deactivator.

Color Stabilizers

The color stability of cracked gasolines is a property which is to a certain degree independent of gum formation. Stable cracked gasolines may be discolored without any appreciable formation of gum. Thus inhibitors which stabilize the gum formation do not stabilize the color.

Moreover, some inhibitors, for instance α -naphthol, have a negative effect on the color stability of inhibited gasolines, especially in sunlight. As a result, the color of the inhibited gasolines after storage may be worse than that of the uninhibited product.

There are special inhibitors which stabilize the color of cracked gasolines and are inactive with respect to gum formation. Brooks⁷ was the first to discover the use of organic amines as color stabilizers. Rogers and Voorhees⁴³ and Sorg⁴⁹ have shown that butyl and amyl amines, when added to cracked gasolines in the very small proportion of 0.003-0.01 per cent, markedly stabilize their color.

Sulphur in Cracked Gasolines

The part played by sulphur in gasolines is out of proportion to the minute quantities of sulphur compounds which are usually present in gasolines. Even a very small content of sulphur in gasolines may be responsible for bad odor, corrosive properties, discoloration in sunlight, and poor response to tetraethyl lead. The total content of sulphur in cracked gasolines depends on the nature of the charging stocks: those having a high content of sulphur yield cracked gasolines rich in sulphur. Table 145 summarizes some data on the sulphur content of crudes and of

Table 145. Sulphur Content in Crude Oils, Straight-Run and Cracked Gasolines.

Crude	—Content of Sulphur in % by Weight in—		
	Crude	Straight-run Untreated Gasoline	Cracked Untreated Gasoline
Pennsylvania	0.04	0.005	0.02
Oklahoma City	0.20	0.01	0.04
Seminole	0.4	0.015	0.03
East Texas	0.3	0.010	0.04
West Texas	0.8	0.12	0.25
Texas Panhandle	0.50	0.055	0.21
Gulf Coast, Placedo	0.15	0.02	0.08
California, Huntington Beach	1.3	0.17	0.8
California, Santa Fé Springs	0.4	0.05	0.2
Arkansas, Smackover	2.0	0.04	0.19
Illinois	0.25	0.03	0.05
Mexico, Panuco	5.2	0.06	1.4
Mexico, Posa Rica	1.8	0.05	0.8
Venezuela, La Rosa	1.8	0.07	0.7
Russia, Grozny	0.2	0.015	0.018
Russia, Baku-Surachany	0.3	0.017	0.066
Iran	0.8	0.08	0.16
Iraq	2.0	0.10	0.34

straight-run and cracked gasolines. These data show that the sulphur content of cracked gasolines is invariably much higher than that of straight-run products from the same crude.

The content of sulphur in the fractions of cracked gasolines usually increases regularly with increasing boiling range. In many cases, however, the percentage of sulphur changes more or less irregularly with increasing boiling range (Table 140) or rises to a maximum and then falls. According to Morrell and Egloff,^{33a} the California cracked gasolines frequently show maxima of sulphur content in the fractions corresponding to 300-350°F. The following data from this communication may be taken as an illustration of such a distribution of sulphur in the fractions (Table 146). However, the uneven distribution of sulphur compounds in the

Table 146. Sulphur in California Cracked Gasolines.

Fraction (% by Vol.)	I Sulphur (%)	II Sulphur (%)
0-10	0.40	0.11
10-20	0.59	0.23
20-30	0.76	0.27
30-40	0.96	0.31
40-50	1.09	0.32
50-60	1.16	0.32
60-70	1.13	0.29
70-80	0.99	0.26
80-90	0.89	0.24

fractions of cracked gasolines is not as marked as in the case of gum-forming constituents.

As has been stated in Chapter 3, the content of sulphur in hydrogenation gasolines is very small, around 0.01 per cent or less. In contradistinction to cracking gasolines, the content of sulphur in hydrogenation gasolines does not depend on the charging stock due to the complete or almost complete decomposition of sulphur compounds in the presence of hydrogen. Gasolines derived from polymerization and thermal conversion of gases are poor in sulphur since the sulphur is previously removed from the charging gases. The average content of sulphur in these gasolines amounts to 0.05 per cent, if the charging stock has been desulphurized.

Various Sulphur Compounds in Cracked Gasolines

In addition to elemental sulphur the sulphur compounds present in cracked gasolines belong to the following classes: hydrogen sulphide, mercaptans, alkyl monosulphides (or thioethers), alkyldisulphides, and thiophenes. The alkyl monosulphides may be aliphatic and cyclic (thiophanes).

The total amount of sulphur in gasolines is expressed in per cents by weight of elemental sulphur. The percentage of mercaptans and other sulphur compounds is also expressed in per cents of elemental sulphur combined in the mercaptans (mercaptan sulphur), etc. The total content of sulphur is determined by the lamp method. A weighed amount

of a gasoline is burned in a standard lamp. The sulphur compounds form sulphur dioxide which is absorbed by the solution of sodium carbonate and determined quantitatively.

According to American and European standards, the percentage of sulphur in motor and aviation gasolines, determined by the lamp method, should not exceed 0.1 per cent. Most of the raw cracked gasolines produced in this country usually have a sulphur content below this specification. Some cracked gasolines, however, such as, for instance, those from California crudes, have an excessive amount of sulphur, frequently even after a heavy treatment with sulphuric acid.

In addition to the determination of total sulphur, there are two qualitative tests pertaining to the sulphur compounds in gasolines: the corrosion and the doctor tests. The corrosion test is carried out by the immersion of a copper strip ($\frac{1}{2}$ in. wide and 3 in. long) in 10 cc. of gasoline in a test-tube for three hours at 122°F. or 212°F. The gasoline is said to pass the corrosion test when the copper strip is not discolored to any noticeable extent.

Elemental sulphur, hydrogen sulphide and to a lesser extent mercaptans react with copper under the test conditions. Monoalkylsulphides and thiophenes do not react at all. Disulphides and particularly polysulphides may give some corrosive effect at 212°F. The corrosion test is usually positive when the percentage of free sulphur is about 0.005 or more. However, many sweetened sour gasolines having a considerable content of free sulphur, up to 0.01-0.02 per cent, may be non-corrosive in the test described.^{27a}

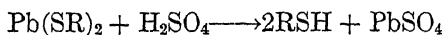
The doctor test is a test for more corrosive sulphur compounds which form lead sulphide from the doctor solution (60 gr. of litharge dissolved in a solution of sodium hydroxide in a liter of water). The test is carried out by shaking in a test-tube 10 cc. of the sample and 5 cc. of the doctor solution for about 15 seconds. A small pinch of sulphur flowers is added, and the mixture is shaken for 15 seconds longer. The discoloration of the sulphur film shows that the gasoline is "sour" (positive doctor test) and *vice versa*. Hydrogen sulphide and mercaptans react easily with the doctor solution, while sulphides, disulphides and thiophenes are inactive. The mercaptans, even in minute quantities, are very sensitive to the doctor test. Gasolines containing 0.001 per cent mercaptan sulphur are usually sour to the doctor test. The amount of mercaptan sulphur in sour gasolines is usually 0.01-0.05 per cent.

A method of complete analysis of various sulphur compounds in gasolines was developed by Faragher, Morrell and Monroe.¹⁹

Hydrogen sulphide is determined by precipitation with an acidified solution of cadmium chloride as cadmium sulphide.

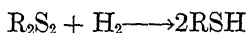
Elemental sulphur is removed by shaking the sample with metallic mercury. The difference in the total amounts of sulphur (by the lamp method) before and after this procedure gives the percentage of elemental sulphur.

The mercaptans are determined by one of two methods: (1) The sample, after the removal of hydrogen sulphide and sulphur, is shaken with alcohol solution of sodium plumbite until it is sweet to the doctor test. The lead mercaptides formed are dissolved in alcohol and removed by the separation of the alcohol solution. The amount of mercaptan sulphur is determined by the difference in the total amounts of sulphur (by the lamp method) before and after this procedure. (2) After removal of hydrogen sulphide and sulphur the sample is dissolved in benzene and treated with a suspension of basic lead acetate. The mercaptans react with the lead acetate, forming the mercaptides $\text{Pb}(\text{SR})_2$ which dissolve in the benzene. The benzene layer containing mercaptides is separated from the aqueous layer in a separatory funnel. A known quantity of 0.1*N* sulphuric acid is added to the benzene layer in the funnel and the funnel is shaken. The mercaptans are regenerated as a result of this reaction:



The excess sulphuric acid unreacted is determined by titration, and the amount of the mercaptans reacted is calculated.

Disulphides are determined in the gasoline freed from hydrogen sulphide and sulphur, by reduction to mercaptans:



The reduction is performed with zinc and acetic or sulphuric acid. After reduction the gasoline is treated with alcoholic sodium plumbite to remove the mercaptans formed. A difference in the amounts of sulphur (by the lamp method) before and after this treatment gives the combined mercaptan and disulphide sulphur. The sulphur in disulphides is found by subtracting the mercaptan sulphur previously determined from the combined mercaptan and disulphide sulphur.

The sulphides present in the gasoline after the last removal of mercaptans and disulphides are removed by treatment with powdered mercurous nitrate. The mercurous nitrate forms with sulphides complex compounds insoluble in gasoline. After removal of these compounds, a lamp determination gives the sulphur in the residuum. The sulphide sulphur is calculated by difference. The residual sulphur is sulphur of thiophenes and, possibly, of some other, unknown sulphur compounds. The analysis of known mixtures by the described method gave very satisfactory results. The data of Table 147 illustrate the distribution of sulphur between the various sulphur compounds in two American¹⁰ and one Russian¹⁴ cracked gasolines. Thus the occurrence of various sulphur compounds in cracked gasolines depends largely on the origin of gasolines. The thiophenes or residual sulphur are predominant in all three gasolines.

McKittrick³¹ studied the sulphur compounds of a cracked California gasoline from Midway crude. The total sulphur content was 1 per cent. The sulphur compounds were primarily concentrated by extraction with

sulphur dioxide. The extract obtained was subjected to a series of fractional extractions, first with aniline and then with ethylene glycol diacetate. The final extract, having a specific gravity 0.900 at 15°C. and containing 5.5 per cent of sulphur (40 per cent of all the sulphur present in the original gasoline), was carefully fractionated. The fractions rich in sulphur were treated with mercuric chloride. The extract contained mostly the derivatives of thiophene: thiophene, methylthiophenes, dimethylthiophenes, and ethylthiophenes. The alkyl thiophenes are predominant. The sulphur compounds from the acid sludge formed in low-temperature refining of cracked gasolines are alkyl sulphides containing 8 carbon atoms of unknown structure, probably cyclic. According to McKittrick, the derivatives of thiophenes are predominant in the California gasoline investigated. It is not known whether the observed predominance of thiophenes is a general property of cracked gasolines or is confined to the gasolines investigated.

Table 147. Sulphur Compounds in Untreated Cracked Gasolines.

Sulphur	California Midway (%)	Smackover (%)	Surachany (%)
Elemental	0.00	0.00	0.005
Hydrogen sulphide	pres.		0.010
Mercaptans	0.02	0.02	0.004
Disulphide	0.11	0.03	0.006
Sulphide	0.02	0.00	0.003
Residula (thiophene)	0.95	0.15	0.088

The above-described method of determining various compounds of sulphur is rather laborious, involving many analytical operations. In practice only the content of mercaptans is sometimes determined, in addition to free sulphur and hydrogen sulphide. In addition to the procedure of Faragher, the determination of mercaptans may be carried out by titration of the sample with the standard solution of copper sulphate in sodium and ammonium hydroxides. The reaction involved is the formation of copper mercaptide $(RS)_2Cu$, resulting in discoloration of the blue solution of the reagent. The details of the operation are described by Francis.²²

Corrosive Properties of Sulphur Compounds

As can be concluded from the tests and special investigations discussed above, the corrosive action of sulphur compounds in gasolines at low temperatures is due mostly to elemental sulphur, H_2S , and somewhat to mercaptans, which react with many metals. The corrosion is accelerated by the presence of water. Monosulphides and thiophenes are non-corrosive. Di- and polysulphides may be slightly corrosive at elevated temperatures. Thus the total amount of sulphur determined by the lamp method is not significant for the corrosiveness of gasolines at low temperatures. The corrosion and doctor tests are more important to an approximate evaluation of the low-temperature corrosiveness of gasolines.

On the contrary, the burning of gasolines containing sulphur compounds produces corrosive sulphur dioxide independently of the chemical characteristics of the compound. The corrosive properties of sulphur dioxide are due to the formation of unstable sulphurous acid in the presence of water at comparatively low temperatures. The sulphurous acid formed may be oxidized further to sulphuric acid. At high temperatures the formation of sulphurous acid does not occur and sulphur dioxide becomes non-corrosive. Thus the corrosive action of sulphur dioxide in engines can be noticed mostly in crank-cases, particularly at low temperatures. The existing standard of the maximal sulphur content in gasolines of 0.1 per cent concerns the use of gasoline as fuel in engines. There are conflicting opinions as to the permissible maximum content of sulphur in motor gasolines as fuels. It has been frequently pointed out that the existing standard of the sulphur content might be considerably increased, and that sulphur dioxide in the combustion gases would not have any appreciable corrosive effect at the moderate and comparatively high temperatures of operation prevailing at least in this country.

Instability of Cracked Gasolines in Sunlight

The instability of cracked as well as straight-run gasolines in sunlight is sometimes closely related to certain sulphur compounds. Some gasolines containing sulphur, when exposed to sunlight, become hazy, lose color and form precipitates. It should be remembered, however, that sunlight also accelerates gum formation by the oxidation of hydrocarbons. Thus both phenomena may occur simultaneously.

The chemical nature of the reactions of sulphur compounds in sunlight is not clearly understood, but it is believed that such compounds as disulphides are oxidized, forming sulphonic acids. The formation of sulphur dioxide and sulphur trioxide also occurs, particularly if elemental sulphur is present in gasoline. Egloff, Morrell, Benedict and Wirth¹⁷ investigated the effect of various sulphur compounds on the color stability of cracked gasolines. A carbon arc lamp was used as a source of the light. While mercaptans had but a little effect on the color stability, free sulphur and disulphides caused color and haze formation in gasolines, both straight-run and cracked. An excess of sulphur and disulphides formed during the sweetening may be responsible for the instability of some cracked gasolines to light. The haziness of gasolines exposed to light is due to the suspended particles which can be removed by filtration. The filtration, however, does not improve markedly the color of discolored cracked gasolines, showing that the color developed upon exposure is due to soluble colored substances. Thus the substances, soluble and insoluble, in gasolines are formed as a result of the action of light on their sulphur compounds.

Removal of Oxygen and Sulphur Compounds

The removal of oxygenated and sulphur compounds from cracked

gasolines is performed by the treating processes described in Chapter 6. The removal of oxygen compounds, such as peroxides and gums, as well as of gum-forming hydrocarbons, does not meet any difficulties due to the reactivity and instability of the compounds and hydrocarbons in question. These constituents may effectively be removed by a light treatment with sulphuric acid, fuller's earth, etc. On the other hand, the unstable gum-forming hydrocarbons can be stabilized by the use of inhibitors, as has been described above.

The removal of sulphur is greatly complicated by the stability and variety of the sulphur compounds present in cracked gasolines, which react in different ways with treating reagents. Fuming sulphuric acid is the most powerful reagent, completely removing mercaptans, monosulphides, disulphides and thiophenes. Commercial sulphuric acid, 66°Bé, in reasonable relative amounts produces only a partial removal of monosulphides, disulphides and thiophenes. More dilute sulphuric acid, 53°Bé, completely loses its action on the sulphur compounds. Caustic solutions remove hydrogen sulphide and part of the mercaptans, being inactive toward other sulphur compounds. Various adsorbents at moderate temperatures are mostly inactive or slightly active with respect to the sulphur compounds present in cracked gasolines, mercaptans, sulphides and disulphides.

Complete removal of sulphur compounds is practically impossible by conventional treatment, if reasonable yields of finished gasoline are expected and reasonable amounts of reagents are used. The treatment only reduces the amount of sulphur compounds and/or converts the most harmful compounds into less objectionable ones, as will be shown in Chapter 6.

Almost complete removal of sulphur compounds from gasolines can be effected either by treatment with powdered metals at 300°C. (572°F.) or by hydrogenation. The use of hydrogenation for desulphurization was discussed above (p. 203). Neither of these methods is employed commercially.

OCTANE RATING OF CRACKED GASOLINES

Octane Numbers of Hydrocarbons

The octane numbers of cracked as well as straight-run gasolines depend on their chemical composition. Theoretically the octane numbers of gasolines can be calculated on the basis of the blending octane numbers of hydrocarbons present in gasolines.

In the following discussion, the data on the octane numbers of hydrocarbons relate to the blending octane values obtained for 20 per cent concentration in a standard fuel. As is known, the blending octane values of hydrocarbons depend on the concentration and octane number of the standard fuel. Thus the data given below on the octane numbers of hydrocarbons have only a relative value.

Various hydrocarbons have different octane numbers depending on their chemical structure. Normal paraffins, with the exception of low molecular weight hydrocarbons, have minimum values of octane numbers. The octane value of normal paraffins very markedly decreases with increasing molecular weight of hydrocarbons. The octane number of normal heptane is accepted as zero. The octane numbers of normal paraffins of a higher molecular weight than heptane are negative. Normal butane and normal pentane have comparatively high octane numbers, 92 and 62 respectively.

The octane numbers of iso-paraffins depend on their structure. The octane numbers of iso-paraffins of similar structure decrease with increasing molecular weight, as in the case of normal paraffins. The octane numbers of iso-paraffins of the same molecular weight increase greatly with increasing branching or centralization of hydrocarbons. For instance, the octane number of octanes varies from -19 for normal octane to 130 for 2,2,3,3-tetramethylbutane. The so-called iso-octane of octane number 100 is 2,2,4-trimethylpentane, a less branched or centralized hydrocarbon than the isomer of 130 octane number.

At the present time, the production of high octane number iso-paraffins is of great importance due to the increasing use of 100-octane number fuels. As has been discussed in Chapter 1, iso-octane of octane number 100 can be produced commercially either by the selective polymerization of iso-octenes followed by hydrogenation or by alkylation of isobutane. Other methods, such as isomerization of normal paraffins, so far have not been developed commercially. The commercial synthesis of such iso-paraffins as 1,2-dimethylethane or 2,2,3,3-tetramethylbutane would produce super-fuels of octane number above 100 without leading.

The octane numbers of olefins usually are higher than those of paraffins of the same structure. For instance, the octane number of 2,2,4-trimethylpentene is about 150, far exceeding that of the corresponding paraffin (100). As in the case of paraffins, the octane numbers of olefins of the same structure decrease with increasing molecular weight and greatly increase with increasing branching at the same molecular weight.

Cyclohexane and cyclopentane have high octane numbers, 85 and 125 respectively. The octane numbers of the derivatives of naphthenes decrease with increasing paraffinic side chains. The branching of the paraffinic side chains has the reverse effect. For this reason the tertiary derivatives of naphthenes have fairly high octane numbers.

The cyclic olefins, or unsaturated naphthenes, have higher octane numbers as compared with saturated naphthenes of the same structure and the same carbon atom number.

The aromatic hydrocarbons have very high octane numbers, 100 and more, which depend only slightly on the molecular weight. The octane numbers slightly increase from benzene to xylenes and slightly decrease for higher homologs.

Thus with the exception of aromatics, the octane numbers of hydro-

carbons of the same structure markedly decrease with increasing molecular weight or increasing boiling point.

Octane Numbers of Cracked Gasolines

The cracked gasolines invariably have higher octane numbers as compared with straight-run gasolines of the same volatility, produced from the same crude. The difference in the octane numbers between mixed-phase-cracked and straight-run gasolines is about 10 or more octane units. Evidently it is due to a higher content of olefins and a lower content of paraffins in cracked gasolines in comparison with straight-run products. As has been stated above, the paraffins that are present in straight-run and cracked gasolines are mostly normal or slightly branched. High paraffinicity of gasolines, straight-run and cracked, results commonly in low octane numbers. The increase in the content of olefins at the expense of paraffins, produced by cracking, gives higher octane numbers.

The octane numbers of cracked gasolines produced by the same method depend on the nature of the charging stock. The paraffinic base crudes and distillates yield cracked gasolines of low octane numbers. On the contrary, the charging stocks from naphthenic and asphaltic crudes produce cracked gasolines of comparatively high octane numbers. The

Table 148. Octane Numbers of Straight-Run and Cracked Gasolines Untreated from the Same Crudes (C.F.R. Motor Method).

Crude	A.P.I. Octane No. of Straight-run Gasoline (400°F.)	Octane No. of Mixed-phase-cracked Gasoline (400°F.)
Pennsylvania, Michigan	42	65
Oklahoma City	48	68
East Texas	54	68
West Texas, Winkler	60	71
Gulf Coast, Mixed	66	74
California, Huntington Beach	57	70
California, Midway	68	74
Illinois	54	67
Arkansas, Smackover	68	73
Venezuela, Cumarebo	52	63
Venezuela, La Rosa	58	70
Mexico, Poza Rica	44	65
Russia, Grozny	42	64
Russia, Baku-Surachany	60	66
Iran	52	69
Iraq	45	67

following data represent the approximate values of octane numbers of straight-run and cracked gasolines produced from the same crudes (Table 148). The octane numbers given in Table 148 pertain to the mixed-phase non-selective cracking at temperatures of about 490-500°C. (896-932°F.). It is understood that somewhat higher octane numbers can be obtained by selective cracking, using more drastic cracking conditions for selective fractions.

The octane number of cracked gasolines produced from the same charging stock and by the same process depends upon the extent of

cracking per pass and the pressure. According to Keith, Ward and Rubin,²⁷ these variables very considerably affect the octane numbers of cracked gasolines. In cracking a Midcontinent gas oil, of 34.9 A.P.I. gravity under 750 lbs. pressure, the octane number of cracked gasolines increased from 62 to 76 (C.F.R. Research Method) when the yield of gasoline per pass increased from 6 to 44 per cent. On the other hand, with the same crack per pass, the octane number decreases on 6 units when the pressure of the process increases from 200 to 750 lbs. The temperature itself, other conditions being equal, does not affect the octane numbers.

The results of Schutt^{48b} seem to be in some contradiction to those of Keith, *et al.*, showing that the octane numbers are influenced by temperature of vapor-phase cracking, but not appreciably by time of reaction. Thus, the octane number of a gasoline increased from 80 to 92 (by C.F.R. Research Method) by increasing the temperature from 1030°F. (7.2 sec. reaction time) to 1160°F. (2 sec. reaction time). The extent of cracking at 1160°F., however, was much greater than at 1030°F.

The octane number of cracked gasolines produced from the same charging stock depends on the temperature-time factor of the process used. The mixed-phase process gives moderate octane numbers of cracked gasolines from 60 to 75, depending on the charging stock. The octane numbers of reformed gasolines are 70 or higher. The octane numbers of vapor-phase-cracked gasolines are considerably higher than those obtained in the mixed-phase process due to a higher content of aromatic and unsaturated hydrocarbons. The influence of the charging stock on the octane numbers of vapor-phase-cracked gasolines is smaller than in the case of the mixed-phase process. The high-temperature vapor-phase cracking or aromatization of petroleum products, including oil gases, produces highly aromatic gasolines of octane number 90-100 from all charging stocks. Catalytic cracking in the presence of clay (the Houdry process) yields gasolines of high octane number, about 78. The content of olefins and aromatics, however, is not high in these gasolines. As has been disclosed on page 151, iso-paraffins are probably responsible for the high octane numbers of catalytically cracked gasolines.

Hydrogenation produces gasolines of lower and higher octane numbers, depending on the temperature conditions of the process, as has been stated in Chapter 3. The high octane numbers of hydrogenation gasolines are due to the high content of aromatic hydrocarbons. On the other hand, the octane numbers of hydrogenated gasolines produced under the same conditions depend upon the original stock, as can be seen from the data of Pier³⁷ given in Table 149.

The polymerized gasolines and those obtained by thermal conversion of gases have octane numbers of around 80. Very high pressure in the thermal conversion of gases reduces appreciably the octane number of the synthetic gasolines produced, as it takes place in conventional cracking of

Table 149. Octane Numbers of Hydrogenation Gasolines Produced from Various Crudes.

Charging Stock	Specific Gravity	Octane Number (C.F.R. Motor Method)
Paraffin wax	0.680	45
Mixed base crude dist.	0.722	64
Asphaltic base crude dist.	0.728	67
Cracked residuum	0.745	74

gas oils. Selectively polymerized and hydrogenated gasolines and catalytically alkylated gasolines (Chapter 1) have the maximum octane numbers. The data on the octane numbers of various synthetic gasolines are summarized in Table 150.

Table 150. Octane Numbers of Synthetic Gasolines Produced by Various Methods (E.P. 400°F. C.F.R. Motor Method).

Process	Octane Number of Cracked Gasoline	Process	Octane Number of Cracked Gasoline
Straight-run distillation	35- 70	High-temperature hydrogenation	75-90
Mixed-phase cracking	60- 75	Catalytic polymerization of gases	80-82
Vapor-phase cracking	70- 80	Thermal conversion of gases	75-80
Reforming	70- 80	Selective polymerization and hydrogenation	90-99
High-temperature vapor-phase cracking (aromatization)	80-100	Catalytic alkylation	85-92
Catalytic (Houdry)	75- 80		
Moderate-temperature hydrogenation	55- 75		

Note: The variations of octane numbers for the same process depend on the charging stock and cracking conditions.

The figures given in Tables 148-150 relate to the octane numbers of unblended synthetic gasolines. The blending octane values may differ from those of the tables. For instance, the catalytically polymerized gasolines have considerably higher octane blending values, around 100, when blended with 50 per cent of a low-octane number gasoline.

The octane numbers of the fractions of cracked gasolines decrease with increasing boiling temperature. As has been stated previously, the content of aromatic hydrocarbons in mixed-phase-cracked gasolines is comparatively small. All other hydrocarbons of cracked gasolines show a strong decrease of octane numbers with increasing molecular weight or boiling range. As a result, the high-boiling fractions of cracked gasolines (as well as of straight-run) have lower octane numbers than the low-boiling ones. Thus the octane numbers of cracked gasolines depend on the boiling range and on the end point, as can be seen from the data of Table 151.

Table 151. Octane Numbers of M.C. Cracked Gasoline of Various End Points.

End Point (°F.)	Octane No. (C.F.R. Motor Method)
300	74
350	70
400	67
437	64

It should be mentioned that the effect of the end point on the octane rating for straight-run gasolines is much greater. The common difference between the octane numbers of 300° E.P. and 437° E.P. straight-run gasolines amounts to 15 units and more. On the contrary, the octane numbers of Houdry gasolines are only slightly dependent upon the boiling range. Thus the naphtha cut may have about the same octane number as aviation or motor gasoline. The octane number of heavy naphthas of highly aromatic gasolines may be higher than that of gasoline due to the high content of aromatics. Some cracked, hydrogenated and synthetic naphthas of sufficiently high octane number, boiling between 300 and 400°F., may be used as safety aviation fuels. As has been stated in Chapters 1 and 3, the octane number of alkylated and hydrogenated naphthas may be as high as 75-95. Aromatic naphthas produced by high-temperature cracking have an octane number of the same order, but are less stable with reference to gum formation than alkylated and hydrogenated naphthas.

The treatment of cracked gasolines may appreciably affect the octane rating. The extent of this effect depends upon the change in the chemical composition of gasolines upon treatment. The drastic treatment with sulphuric acid may considerably reduce the octane number of a treated gasoline due to the decrease in the content of olefins and aromatics. The treatment of adsorbents, such as fuller's earth, is more selective and affects only the most unstable unsaturates which are usually present in cracked gasolines in small quantities. As a result, the octane numbers of cracked gasolines are not affected by the treatment with adsorbents. The effect of the chemical treatment of cracked gasolines will be discussed in detail in Chapter 6.

It should be mentioned that the C.F.R. Motor method underrates cracked and polymerized gasolines in determining the octane values as compared with actual road performance of the cars. The difference between the road and C.F.R. Motor method tests is usually no less than 3 units. This should be kept in mind when the octane numbers of straight-run gasolines are compared with those of cracked gasolines (Table 148).

The Influence of Sulphur and Oxygen Compounds on Octane Numbers

The influence of sulphur and oxygen compounds formed in oxidation on the octane numbers of cracked gasolines should not be overlooked. The presence of sulphur compounds slightly decreases the octane numbers of gasolines even at very small concentrations of the compounds. Birch and Stansfield² investigated the effect of various sulphur compounds on the octane number of a heptane-hexane blend, of octane number 65. The addition of elemental sulphur and some sulphur compounds in the proportion of 0.1 per cent of sulphur decreased the octane number of the blend by 0.2 units. Elemental sulphur, mercaptans and ethyl trisulphide had

the maximum depressing effect. Monosulphides, thiophene, and carbon disulphide were inactive. Schulze and Buell⁴⁸ give the following data on the effect of mercaptans and disulphides on the octane number of a gasoline (Table 152). Thus the effect of mercaptans and disulphides is about the same on the gasoline investigated.

Table 152. Effect of Mercaptans and Disulphides on Octane Number.

Compound Added	Amount as Sulphur (%)	Octane No.
None		50.8
Methyl mercaptan	0.044	49.8
Methyl disulphide	0.050	49.9
Ethyl mercaptan	0.042	50.0
Ethyl disulphide	0.043	50.1
<i>n</i> -Butyl mercaptan	0.040	49.9
<i>n</i> -Butyl disulphide	0.038	49.9

The octane numbers of stable cracked gasolines do not change during storage. On the contrary, the unstable gum-forming gasolines gradually deteriorate with respect to octane number. The decrease in octane number is accompanied by gum formation. This phenomenon is due to the oxidation of high-octane number unsaturated hydrocarbons to gum and to the formation of peroxides that are knock inducers.

The decrease in octane number in storage may be as high as 10 units and more in the advanced stage of deterioration. The following example¹⁶ gives a clear idea of the deterioration of a cracked gasoline (Table 153). The decrease in octane number was a result of oxidation and a heavy formation of gum.

Mardles and Moss²⁹ found that there is an approximate relationship between the increase in the dissolved gum content and decrease in octane number (Table 154).

The decrease in octane number of the previous example (Table 153) is fairly close to what would be expected from the data of Table 154.

Table 153. Gum Formation and Octane Number of Cracked Gasolines After Storage.

	Color Saybolt	Copper-Dish Gum (mg./100 cc.)	Air-Jet Gum (mg./100 cc.)	Octane No.	Induction Period (minutes)
Cracked Gasoline, Untreated	19	85	4	77	15
Same after 6 months	11	842	538	65	

Table 154. Increase in Gum Content and Decrease in Octane Number of Cracked Gasolines.

Increase in Dissolved Gum Content (mg./100 cc.)	Decrease in Octane No., Ethyl Gasoline Corporation Engine, Series 30, 100°C. Jacket Temperature
20	2.5
150	5
100	7
200	10
300	12.5
400	14

Susceptibility of Cracked Gasolines to Tetraethyl Lead

The data summarized in the previous section show that the octane numbers of various cracked gasolines range on the average between 60 and 85. By the term "cracked gasolines" is meant all commercial gasolines produced by any method of cracking, hydrogenation, polymerization and thermal conversion of gases. Gasolines of higher octane numbers (90-100) can be produced only as a result either of the synthesis of certain iso-paraffins or of the aromatization of oil products and gases. Both methods are rather expensive and are used for the production of special premium fuels. The high-octane number gasolines are manufactured in commercial practice by the addition of small percentages of tetraethyl lead to straight-run and cracked gasolines. Even the production of standard motor gasoline of octane number 70-72 from common straight-run and mixed-phase-cracked gasolines usually requires some addition of tetraethyl lead. The susceptibility or response to tetraethyl lead, *i.e.*, the effect produced, for instance, by 1 cc. of tetraethyl lead per gallon, is a very important property of cracked gasolines such as motor fuels.

The susceptibility of gasolines to tetraethyl lead depends mainly on two factors: their initial octane number and their chemical composition. The lower the octane number of a gasoline, the greater is its response to tetraethyl lead, and *vice versa*. As a result, tetraethyl lead is most effective in small concentrations, and its effectiveness rapidly decreases with increasing concentration. The leading of high-octane number gasolines also produces a comparatively slight effect; many cc. of tetraethyl lead liquid are required to increase the octane number, for instance, from 80-85 to 100.

Two gasolines of the same octane number may have different lead susceptibilities depending on the chemical nature of the hydrocarbons. Garner and Evans²⁴ investigated the influence of the nature of hydrocarbons on the lead susceptibility. The experiments were made with 20-per cent solutions of various hydrocarbons in a standard fuel of octane number 50. The hydrocarbons added were α -olefins, cyclopentanes, cyclohexanes and aromatics. The engine employed was the Ethyl Gasoline Corporation Series 30 model; the jacket temperature was 212 and 300°F.

The results of this investigation may be briefly summarized as follows. The increasing order of lead susceptibility is: aromatics, cyclohexanes, cyclopentanes, α -olefins. In the same class of hydrocarbons, the lead susceptibility increases with increasing molecular weight, as the length of the paraffin side chain increases and the octane number falls.

The high lead susceptibility of α -olefins seems to be a peculiar property of these unsaturates. Other unsaturates present in cracked gasolines usually have poor response to lead. Thus polymerized gasolines, highly unsaturated, are of very poor lead susceptibility, which is greatly

improved by hydrogenation. The lead susceptibility of unsaturates of cracked gasolines may be poorer than that of aromatics.

Campbell, Signaigo, Lovell and Boyd⁹ have found that some unsaturated cyclic hydrocarbons, including cyclopentadiene derivatives and aromatic hydrocarbons with unsaturated side chains, have an increase in knock intensity in the presence of tetraethyl lead (1 cc. per gallon). In other words, the tetraethyl lead acts in these hydrocarbons as a knock inducer. These hydrocarbons, present in small amounts in some cracked gasolines, particularly from the vapor-phase process, may affect the response to tetraethyl lead. The lead susceptibility of paraffin hydrocarbons is higher than that of all other hydrocarbons. Thus, natural gasolines containing mostly paraffins have maximum values of lead susceptibility.

The influence of sulphur compounds on lead susceptibility is of great importance. The effect of ethyl disulphide on the lead susceptibility of a heptane-octane blend (octane number 65) is shown by the data of Birch and Stansfield² given in Table 155.

Table 155. Effect of Diethylsulphide on Lead Susceptibility of Heptane-Octane Blend, Octane Number 65.

Concentration of Disulphide (%S)	Octane No. after Leading, 3 cc. Tetraethyl Lead/Gal.	Increase in Octane No. after Leading, 3 cc. Tetraethyl Lead/Gal.
0.00	84	19
0.05	78	13
0.10	76	11
0.20	73	8

The influence of mercaptans and disulphides on lead susceptibility is also illustrated by the data of Schulze and Buell⁴⁸ (Table 156).

Table 156. Effect of Mercaptans and Disulphides on Lead Susceptibility of Gasoline.

Compound Added	Amount as Sulphur (%)	Octane No. of Gasoline	Same with 1 cc. T.E.L./Gal.	Lead Response per 1 cc. T.E.L./Gal.
None	0.000	50.8	63.7	12.9
Methylmercaptan	0.044	49.8	58.9	9.1
Methylsulphide	0.050	49.9	58.9	9.0
Ethylmercaptan	0.042	50.0	58.9	8.9
Ethylsulphide	0.043	50.1	59.1	9.1
n-Propylmercaptan	0.040	49.9	58.9	9.0
n-Propylsulphide	0.038	49.9	58.8	9.1

Thus mercaptans and disulphides have about equal depressing effect on lead susceptibility. The depressing effect of doctor sweetening on lead susceptibility is explained by the trisulphides that may be formed in the sweetening process. The trisulphides seem to be very active in depressing the lead susceptibility. The loss in octane number after doctor sweetening usually is 0.5-3.0 units. An excess of sulphur in doctor sweetening may be particularly detrimental to lead susceptibility.

The latest data of Schulze and Alden^{48a} are of particular interest with reference to the effect of small amounts of sulphur on lead susceptibility.

A Borger natural gasoline, containing 0.037 per cent sulphur, was desulphurized to 0.008, 0.004 and 0.002 per cent. The octane numbers and lead response of the initial and desulphurized gasolines are as follows:

	% Sulphur:	Initial	Desulphurized		
		0.037	0.008	0.004	0.002
Clear		67.2	69.5	69.6	69.7
1 cc. tetraethyl lead		75.6	80.0	81.0	81.4
3 cc. " "		82.1	85.3	86.8	87.5
6 cc. " "		86.6	91.2	92.8	93.2

These figures clearly show that the desulphurization of gasolines to the minimum sulphur content is of importance for producing high-octane number fuels.

The depressing effect of sulphur compounds on lead susceptibility should be attributed to the reaction of these compounds with tetraethyl lead in the burning mixture, resulting in the formation of lead sulphide, inactive as a knock suppressor.

Table 157. Lead Susceptibility of Various Straight-run and Cracked Gasolines (400°F. End Point).

Process	Octane No.	—Octane No. After Leading With T.E.L., cc./Gal.—					
		0.5	1.0	2.0	3.0	4.0	6.0
Natural gasoline (sp. cut)	73		82	86	89		93
Straight-run Pennsylvania	42		58	66	70		
Straight-run California	60		69	73	75.5		
Mixed-phase	67		73.5	76.5	79		
Vapor-phase	78		82	84	85		
Reforming	70		75	77	78		
Catalytic (Houdry)	77.5		84.0	86.6	88.5	8.8	
High-temp. vapor-phase	85		88.5	90	91		
Moderate-temp. hydrogenation	66.1	73.1	77.9	80.6			
High-temp. hydrogenation	85.0		88.5	89.0	90.0		
Catalytic polymerization	81.0		83.5	84.5	85.0		
Thermal conversion of	79.0		84.6		88.5		

The susceptibility of cracked gasolines to tetraethyl lead may be approximately estimated on the basis of the chemical composition. Hydrogenation gasolines produced at moderate temperatures, rich in paraffins, are very susceptible to tetraethyl lead. The mixed-phase-cracked gasolines from paraffinic and mixed base crudes follow the hydrogenated gasolines in the order of lead susceptibility. The vapor-phase-cracked gasolines, particularly high aromatic gasolines of high-temperature processes, have poor lead susceptibility due to a high content of unsaturated and aromatic hydrocarbons. A considerable content of sulphur may affect appreciably the computation of lead susceptibility. The following data illustrate the lead susceptibility of various cracked gasolines (Table 157).

The lead susceptibility of cracked gasolines may be affected by their treatment. Treatment with adsorbents does not affect the susceptibility or the octane numbers of cracked gasolines. As will be shown in Chap-

ter 6, treatment with sulphuric acid increases lead susceptibility, while doctor sweetening may have an adverse effect.

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Chapter 6

Treatment of Cracked Gasolines

The wide use of inhibitors or antioxidants has considerably reduced the extent of chemical treatment of cracked gasolines. At the present time a large proportion of cracked gasoline is only sweetened and inhibited. Nevertheless the part played by chemical treatment remains relatively important to unstable gasolines, gasolines of high sulphur content and high-grade products such as aviation fuels, special naphthas, etc.

Stabilization of Cracked Gasolines

The raw cracked gasolines obtained directly from cracking units are not satisfactory as motor fuel. First of all they usually contain an excess of low-boiling fractions, including C_4 , C_3 and even a small quantity of C_2 hydrocarbons. The Reid vapor pressure of such gasolines is much higher than allowed by specifications (12 pounds per square inch gauge or lower), resulting in high losses in storage and in vapor lock in operation.

The excessive amount of the low-boiling fractions in cracked gasolines is due to the dissolution of cracked gases in gasolines. Raw cracked gasolines are particularly rich in low-boiling fractions when condensation takes place under high pressures, as in the Dubbs and Holmes-Manley units.

The first process is the stabilization of raw cracked gasoline. This operation is performed in conventional stabilizers either directly attached to the cracking unit or located outside it, if the refinery has a centralized stabilizer for many processing units. The description of stabilizers is beyond the scope of this volume.

As a result of stabilization, the cracked gasoline contains only the allowable proportion of butanes and butenes conforming to the specification of vapor pressure. The total amount of butanes and butenes in stabilized cracked gasolines usually is about 5-10 per cent by volume. Hydrocarbons of C_2 and C_3 structure are removed completely or almost completely in stabilization. Another result of stabilization is the production of the waste low-boiling fractions and gases, containing predominantly C_2 , C_3 and C_4 hydrocarbons, which will be considered in Chapter 7.

Stabilized cracked gasolines conforming to the specifications of the vapor pressure and A.S.T.M. distillation may be unsatisfactory as motor fuel on account of bad odor, poor color, gum-forming properties and excessive sulphur content. If necessary, all these may be improved by chemical treatment.

The chemical treatment of cracked gasolines may be appreciably

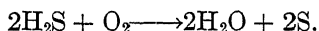
simplified by the separation of the cracked gasoline into light and heavy fractions, of which only the latter is subjected to a comparatively expensive chemical treatment. The light gasoline fraction frequently does not require any treatment, or is subjected to a light washing with soda solution. The light fraction may amount to as much as 30-40 per cent of the total cracked gasoline. By this means, an appreciable saving in reagents as well as a reduction of treatment losses may be obtained.

As has been stated on page 318, the sulphur compounds may be concentrated in certain high-boiling fractions. Separation of these sulphur-rich fractions and selective treatment may also result in a great saving in reagents and treatment losses.

The end point of raw cracked gasolines should correspond to the specification, unless a treatment with sulphuric acid is used for the final refining. In the latter case, the end point of raw gasoline or pressure distillate may be higher than required by specification, since treatment with sulphuric acid, which produces high-boiling fractions, is followed by redistillation. No other methods of treatment change the end point of treated gasolines. Thus in these cases, rerunning of the treated distillate is avoided, if the end point of the raw product conforms to specification.

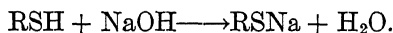
Only those methods of treating cracked gasolines which are in practical use are described in this chapter.

Treatment with Caustic Soda.—Treatment with caustic soda removes hydrogen sulphide which was formed in cracking and dissolved in the cracked gasoline upon condensation. The hydrogen sulphide present in cracked gasolines exposed to air is oxidized, forming sulphur according to the equation:



As a result, hydrogen sulphide is converted into elemental sulphur which cannot be removed by caustic. Thus cracked gasolines containing hydrogen sulphide should be treated with caustic immediately after stabilization. The removal of hydrogen sulphide with caustic is complete.

Mercaptans are only partially removed by caustic solutions. The reaction between sodium hydroxide and mercaptans leads to the formation of mercaptides:



The reaction, however, is reversible, and mercaptides are readily hydrolyzed with water forming mercaptans, according to Borgstrom, Dietz and Reid.⁵ The reaction of the formation of mercaptides is almost complete for the low molecular weight mercaptans, including propylmercaptan (boiling point 68°C.). Thus the mercaptans can be removed to a great extent by caustic solutions from low-boiling gasolines such as light natural gasolines, or butane fractions.

A light, cracked naphtha was treated by Happel and Robertson¹⁰ with caustic soda solution containing 0.05 lb. per gallon at 40°F. in a

two-stage countercurrent unit. The total amount of mercaptan sulphur in the raw naphtha was 0.0128 lb./gal. and after the two stages of treatment was only 0.0032 lb./gal., *i.e.*, the removal of mercaptans amounted to 75 per cent of the original.

Weak caustic solutions are mostly used for the removal of mercaptans. Ridgway²² recommended the use of more concentrated solutions, but the concentration should not exceed 15 per cent.

Vesselovsky and Kalichevsky²⁶ recommended the caustic treatment in absolute alcohol solutions. The hydrolysis of the mercaptides formed is strongly reduced in alcohol solutions, and the removal of mercaptans is carried out quantitatively. Brandt and Hougen⁶ applied this method to the refining of cracked furnace oils.

Yabroff and Border²⁸ have found that the removal of mercaptans from gasolines with sodium hydroxide solution may be almost quantitative in the presence of certain organic compounds (solutizers). Potassium isobutyrate is a very active "solutizer." Typical solutions employed contain from 4 to 6 mols of potassium hydroxide and 3 mols of isobutyrate salt per liter. Many cracked gasolines containing as much as 0.04-0.05 mercaptan sulphur, particularly of lower end point, may be sweetened by this method. According to Yabroff, the solubility of the unneutralized mercaptan in aqueous phase is of primary importance for the separation of mercaptans with caustic solutions. The unneutralized mercaptan is salted out by the sodium hydroxide. The solutizers increase the solubility of the unneutralized mercaptan in the aqueous phase and prevent the salting-out effect of sodium hydroxide. The solutizer method is being employed at present on a commercial scale.

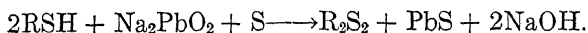
Other sulphur compounds, as well as gum and gum-forming constituents, are not affected by treatment with caustic. The odor is improved due to the removal of hydrogen sulphide and part of the mercaptans. Thus the caustic treatment is used for cracked gasolines which do not require more drastic methods of refining. On the other hand, the treatment with caustic is successfully used as a pretreatment to remove hydrogen sulphide and part of the mercaptans. It is understood that the caustic treatment is followed by washing with water.

Gasolines treated with caustic are frequently inhibited by antioxidants. Inhibition is not used for catalytically cracked gasolines (Houdry process), or for hydrogenation gasolines.

Sweetening of Cracked Gasolines

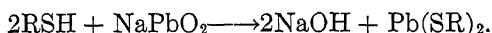
Sweetening is employed for the removal of mercaptans which are objectionable as highly corrosive constituents. In addition, mercaptans impart an unpleasant odor. At present sweetening is the most widely used treating operation; practically all cracked gasolines are subjected to it either before inhibition, without further treatment, or after the treatment by the methods described below.

Doctor Treatment.—The old and still most generally used method of sweetening is treatment with the doctor solution, *i.e.*, a solution of sodium plumbite with addition of sulphur. This reagent converts mercaptans to alkyl disulphides according to the equation:

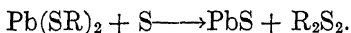


As the equation shows, elemental sulphur, formed in the oxidation of hydrogen sulphide, may be removed by this reaction. The quantity of sulphur present in raw cracked gasolines usually is not sufficient for the reaction, and a small amount of sulphur is therefore added to the doctor solution. The addition of sulphur should be made with extreme care so as not to increase the sulphur content of the finished gasoline, which results in lowering its octane number and decreasing its lead susceptibility. Corrosiveness is also appreciably increased by an excess of sulphur.

The equation given above represents only the final result of the reaction. Actually it is much more complicated. In the first stage mercaptides of lead are formed:



In the second stage the mercaptides react with sulphur forming disulphides:



Thus in the absence of sulphur, mercaptans form only lead mercaptides which are partially soluble in gasolines, imparting a yellow color.

Ott and Reid^{19a} proved that the mercaptides formed may react with sulphur to yield compounds of the types $\text{Pb}(\text{SR})(\text{SSR})$, and $\text{Pb}(\text{SSR})_2$. These compounds are unstable and may be decomposed with formation either of disulphides or tri- and polysulphides.

Doctor sweetening does not actually remove the mercaptans, but transforms them into disulphides which are less harmful than mercaptans with respect to corrosiveness and odor. The total content of sulphur usually is not changed after sweetening. Disulphides, however, have much higher boiling points than volatile mercaptans, and the part of disulphides formed boils above the end point of the original gasoline; thus redistillation of the treated gasoline may decrease the total content of sulphur in gasolines rich in mercaptans. Such a case seems to be rather hypothetical, since the content of mercaptans is usually comparatively small. On the other hand, sweetening is carried out as a final operation after redistillation. Other sulphur compounds are not affected by the doctor treatment.

Table 158 contains a typical sulphur analysis of a gasoline before and after sweetening, according to Happel and Robertson.¹⁰

The concentration of the caustic soda solution used for sweetening is from 10 to 30°Bé. The concentration of litharge (PbO) depends upon the concentration of caustic soda, being about 3 per cent in a 30°Bé.

Table 158. Sulphur Analysis of Gasoline Before and After Sweetening.

	Sulphur in Sour Distillate (% by wt.)	Sulphur in Sweetened Distillate (% by wt.)
Elemental sulphur	0.000	0.010
Mercaptan sulphur	0.018	0.000
Residual sulphur	0.151	0.170
Total sulphur	0.169	0.180
Sulphur added	0.016	
Total	0.185	0.180

solution and less in less concentrated solutions. Sulphur, packed in a small tower, is gradually dissolved in a side stream of the raw gasoline. The sulphur solution in gasoline is added to the product. The temperature of the process is between 80 and 90°F. (27-32°C.). When the gasoline, litharge-caustic and sulphur solution are combined, the mixing should be thorough and effective. The mixing period varies from 30 seconds to several minutes. In the continuous operation the settling takes place in a settling drum, after which the gasoline is washed with water.

The doctor treatment is usually performed after the treatment with sulphuric acid and redistillation, if sulphuric acid is used for refining. The disulphides formed in the sweetening are comparatively unstable and may be decomposed under rather severe conditions of the chemical treatment and redistillation. In other methods of treating, such as with clay or zinc chloride, doctor sweetening also is the final operation.

The doctor treatment usually affects the octane number and lead susceptibility of treated gasolines, as has been discussed above, p. 331. This phenomenon is ascribed to the formation of alkyl polysulphides in the presence of an excess of sulphur. Theoretically, and sometimes in practice, it may be avoided by scrupulous control of the process.

Doctor sweetening properly performed frequently improves the color stability of cracked gasolines. In these cases the content of copper dish gum is appreciably decreased after doctor sweetening, resulting also in some improvement of storage stability. Since doctor sweetening does not remove any unstable unsaturates, it is not easy to understand the mechanism of this phenomenon. It is possible that the very small amount of elemental sulphur present in sweetened gasolines has an inhibiting effect on the oxidation reactions.

The content of mercaptans in cracked gasolines to be sweetened varies from 0.001 to 0.05 per cent of mercaptan sulphur. Conforming to this, the consumption of litharge may vary from 10 to 500 lbs. per 1000 barrels of gasoline. Thus a preliminary treatment with sodium hydroxide solution for the partial removal of mercaptans is highly recommended, particularly for cracked gasolines rich in mercaptans. A considerable saving in litharge may be obtained as a result of preliminary caustic washing.

The recovery of spent plumbite may be an important operation for the plants consuming considerable amounts of this reagent. Lead sul-

phide obtained after the doctor treatment is oxidized to lead sulphate which is dissolved in caustic solution. The oxidation may be effected by various methods:

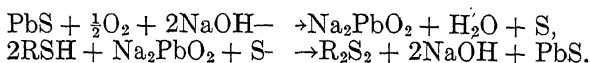
(1) By blowing air at 175-200°F. in the presence of sodium hydroxide:
 $\text{PbS} + 2\text{O}_2 + 4\text{NaOH} \rightarrow \text{Na}_2\text{PbO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}.$

(2) By the action of chlorine in aqueous solution: $\text{PbS} + \text{Cl}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{PbO}_2 + \text{S} + 2\text{HCl}.$

(3) By the reaction with dilute sulphuric acid: $\text{PbS} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{S}, \text{PbSO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2\text{PbO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}.$

According to Altschuler and Graves,² the chemical cost of the doctor treatment is \$19.84 without recovery of spent plumbite, and \$2.70 with recovery per 1000 barrels of gasoline containing 0.01 per cent of mercaptan sulphur.

Lead Sulphide Sweetening.—Litharge may be replaced by lead sulphide in the sweetening process. The Stratco Lead Sulphide process described by Altschuler and Graves² uses lead sulphide in caustic solution in the presence of air. The reactions involved in the process may be summarized as follows:



Thus the oxidation of lead sulphide in caustic produces the doctor solution which transforms mercaptans into disulphides by the customary reaction of sweetening. The lead sulphide regenerated in the second stage is repeatedly oxidized, and the process is theoretically continuous.

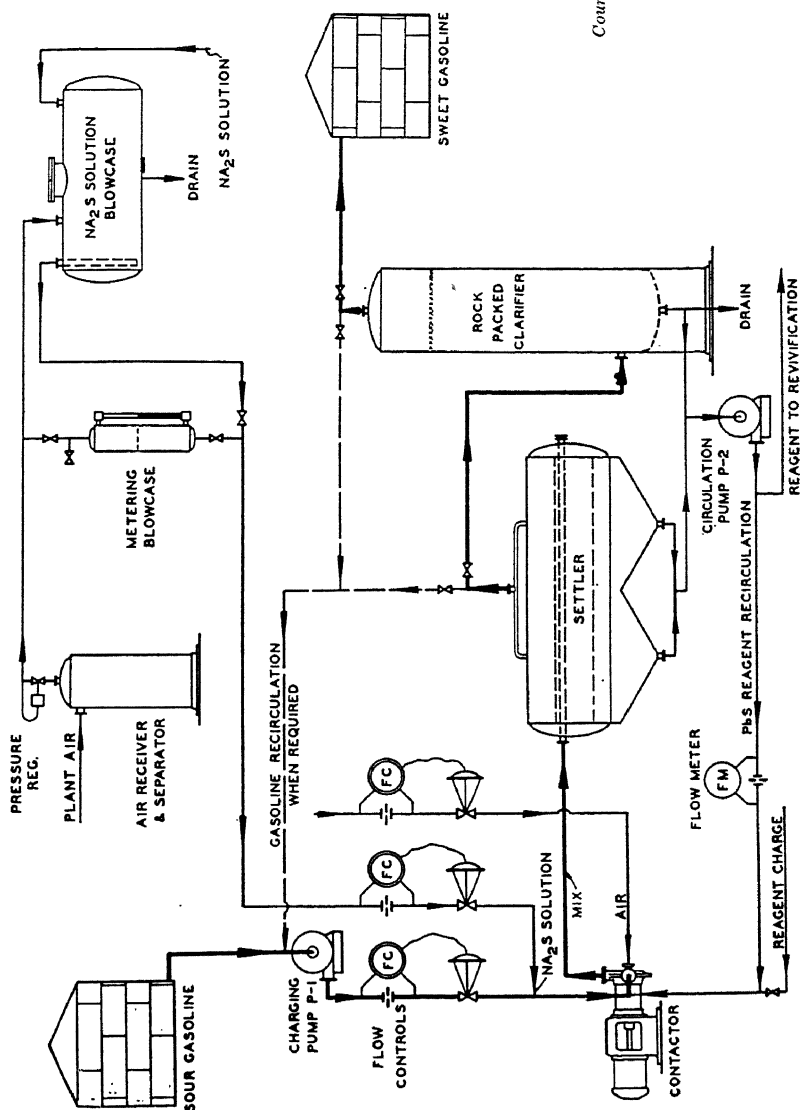
The scheme of the process is given in Figure 48. Lead sulphide is primarily produced by the reaction between lead reagent and sodium sulphide. Sour gasoline, the reagents, recirculated lead sulphide reagent, and air are mixed and reacted in a contactor and then separated in a settler. If necessary the gasoline is recirculated for the repeated operation.

An addition of sulphur is not used in the process, and by this way the troubles caused by an excess of sulphur in the doctor solution are completely avoided. The octane numbers of gasolines treated by the lead sulphide process are reported to be higher by 0.5 unit than in the case of the conventional doctor treatment. A main advantage of the process, however, is the recovery of the reagent *in situ*, which results in an appreciable saving. The cost of chemicals required for sweetening a gasoline containing 0.01 per cent mercaptan sulphur is claimed to be \$1.60 per 1000 barrels. Lead sulphide sweetening does not affect other sulphur compounds present in gasoline.

Copper Sweetening Process.—The Perco Copper Sweetening process replaces the doctor solution with a solution of copper chloride. The process has been described by Albright.¹ Mercaptans are transformed into disulphides without addition of sulphur:



FIGURE 48.—Stratco
Lead Sulphide Proc-
ess.

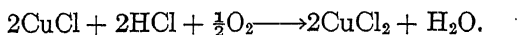


*Courtesy "Refiner and Natural
Gasoline Manufacturer".*

Hydrogen sulphide reacting with copper chloride should be removed before the treatment.

The cracked gasoline is intimately mixed in equal volumes with copper chloride solution. Separation of the treated gasoline from the copper chloride solution takes place in a separating tank. The sweetened gasoline, containing traces of copper compounds, is treated in the second stage with aqueous solution of sodium hydroxide and sodium sulphide. The copper compounds soluble in gasoline form copper sulphide and are removed. The complete removal of the traces of copper salts is very important, since copper salts are very powerful catalysts of oxidation, and even minute quantities of copper markedly deteriorate the stability of cracked gasolines (page 316). A content of copper equal to one part per 1,000,000 parts of cracked gasoline makes gasoline unstable. The use of deactivators to offset the catalytic action of the traces of copper (page 316) is recommended.

The spent copper solution containing cuprous chloride is oxidized with air, resulting in a complete regeneration of copper chloride according to the equation:



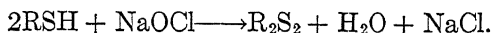
Very easy regeneration of the spent reagent, as well as elimination of the use of free sulphur, are the advantages of the Perco process. Other sulphur compounds, as well as gum and gum-forming constituents, are not affected by copper sweetening.

A modification of the method discussed above has been described by Benedict, Dryer, Morrel and Egloff³ as the U.O.P. sweetening process. This process employs the mixture of cupric sulphate and ammonium chloride impregnated into a carrier, such as fuller's earth or firebrick. The operation is carried out by seeping the gasoline to be sweetened through a percolation tank filled with the reagent on the carrier.

The Hypochlorite Process.—The hypochlorite process is frequently used for natural and straight-run gasolines and rarely for cracked naphthas. The chlorination of hydrocarbons is avoided by the use of alkaline solutions. Under these conditions, hypochlorite attacks mainly sulphur compounds, oxidizing them to sulphonic acids and sulphones. Hydrogen sulphide, being oxidized to sulphur, should be first removed by caustic treatment. Elemental sulphur and thiophenes do not react with hypochlorite. The unsaturated hydrocarbons forming gum are not attacked by hypochlorite under the conditions employed for the removal of sulphur compounds. The sulphonic acids and sulphones formed are partially dissolved in the distillate and are finally removed from the treated distillate by washing with soda solution and water.

The hypochlorite process differs essentially from the methods of sweetening described above which remove only mercaptans. The removal of sulphur compounds may be much more complete by the use of

hypochlorite. However, under mild conditions of the treatment, mercaptans may be oxidized to disulphides according to the equation:



In this case the hypochlorite process practically gives the same results as other methods of sweetening.

The hypochlorite process is not employed for the treatment of cracked gasolines because of the instability of treated cracked products. It is claimed, however, that satisfactory results were obtained by the hypochlorite treatment of Iranian cracked gasolines when very dilute solutions of calcium hypochlorite (0.07*N* available chlorine in saturated lime-water) were used as well as an efficient washing.⁴

Treatment with Sulphuric Acid

Chemistry of Sulphuric Acid Treatment.—The action of sulphuric acid on cracked gasoline is extremely complicated and proceeds in a number of directions. Sulphuric acid may react with aromatic and unsaturated hydrocarbons, sulphur compounds and resinous materials. Under proper conditions, it may remove most of the objectionable constituents of cracked gasolines.

The aromatic hydrocarbons are converted into sulphonic acids on reacting with sulphuric acid. Inasmuch as aromatics are valuable gasoline ingredients, such conditions must be chosen that the sulphuric acid will not react with the aromatics. This may be accomplished by using either dilute sulphuric acid or a comparatively small amount of the reagent. In the latter case, small amounts of sulphuric acid react first with the unsaturated hydrocarbons. The concentration of the acid is lowered by this first reaction sufficiently to avoid any reaction with the aromatics. The content of aromatic hydrocarbons is affected to a very small extent by the treatment with 66°Bé. sulphuric acid, at least if a reasonable quantity of the reagent is used. Unsaturated hydrocarbons react with sulphuric acid in various ways, forming sulphuric acid esters, alcohols, polymers and gums.

Sulphuric acid esters may be of two varieties which are represented by the formulas RHSO_4 and R_2SO_4 , the latter type being naturally obtained in the case of an excess of olefins. These dialkyl esters are not soluble in sulphuric acid or acid sludge, but are soluble in gasoline and must therefore be removed from the gasoline after the sulphuric acid treatment.

The hydrolysis of the esters formed to alcohols is of secondary importance due to the predominance of polymerization reactions, as has been discussed on page 43. If the alcohols are formed from low molecular weight olefins, they are dissolved and removed in the acid sludge. Most of the olefin content is polymerized to polymers, mostly dimers and trimers. The polymers have a double bond and are therefore also un-

saturated hydrocarbons. They do not react further with sulphuric acid, however, due to the fact that high molecular weight unsaturated hydrocarbons with a double bond are generally less active and more resistant.

The polymers are insoluble in sulphuric acid and are transferred into the gasoline in the same way as the dialkyl esters, increasing the specific gravity of the gasoline and its final boiling point. Therefore the polymers formed must also be removed from the cracked gasoline after the acid treatment.

Since the unsaturated hydrocarbons (olefins), except diolefins, are valuable ingredients in cracked gasolines, a vigorous treatment should be avoided as well as long duration of the treating process or the use of large amounts of sulphuric acid and elevated temperatures. Diolefins react with sulphuric acid first and, theoretically, the treating conditions should be such that the action of the sulphuric acid is limited to only those compounds which must be removed.

The extent to which the formation of polymers and dialkyl esters caused by the sulphuric acid treatment acts on the final boiling points of gasolines is shown by the data of Morrel¹⁸ (Table 159).

Table 159. Cracked Gasolines from California Fuel Oil (1) and Midcontinent Gas Oil (2).

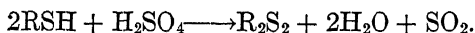
	Untreated	Treated With			
		2½ lbs. per bbl.	5 lbs. per bbl.	10 lbs. per bbl.	10 lbs. per bbl.*
(1)					
A.P.I. Gravity	55.9	56.2	56.3	56.2	55.3
I.B.P. (°F.)	109	109	111	115	120
E.P. (°F.)	405	413	419	442	453
(2)					
A.P.I. Gravity	59.9	58.6	58.3	58.3	57.5
I.B.P. (°F.)	108	110	112	116	121
E.P. (°F.)	405	428	435	442	450

* Three applications of acid: 2½ lbs., 2½ lbs., and 5 lbs.

The reaction between diolefins, aliphatic and cyclic, and sulphuric acid is much more vigorous than in the case of olefins. The mechanism of this reaction is completely obscure. Tars and resins are the final products of the reaction. These most objectionable unsaturated hydrocarbons can be removed more or less selectively from cracked gasolines, if the conditions of the treatment (relative amount of sulphuric acid, concentration, temperature) are comparatively mild.

A great variety of sulphur compounds may be present in cracked gasolines as shown in Chapter 5, and the action of sulphuric acid on them is very complicated. These reactions cannot be considered as fully explained.

Mercaptans may react with sulphuric acid, forming disulphides according to the equation:



Wood, Lowy, and Faragher²⁷ investigated this reaction and found that appreciable desulphurization of a naphtha containing mercaptans

takes place only with high percentage of the acid, not less than 40 per cent by weight. Thus mercaptans are not attacked, or are attacked to a very small extent, by sulphuric acid under usual conditions of the treatment.

Monosulphides and disulphides are partially removed by sulphuric acid which has mainly a solvent action upon these compounds. The relative amount of sulphuric acid used in commercial operation may remove an appreciable part of mono- and disulphides.

Thiophenes react with sulphuric acid and form corresponding sulphonic acids, as aromatic hydrocarbons. The removal of thiophenes is only partial, unless a very high relative amount of sulphuric acid is used. Youtz and Perkins²⁹ published some data on the solubility of various sulphur compounds in sulphuric acid. In each case 100 cc. of the solution were treated twice in succession with 3 cc. of strong sulphuric acid (Table 160).

Table 160. Treating Various Sulphur Compounds with Strong Sulphuric Acid.

Compound	Original Solution	After First Acid Treatment Per cent	After Second Acid Treatment
Ethyl sulphide	0.477	0.041	0.045
Iso-amyl sulphide	0.586	0.185	0.100
Heptyl sulphide	0.438	0.089	0.010
Allyl sulphide	0.624	0.051	0.038
Phenyl sulphide	0.507	0.416	0.464
Benzyl sulphide	0.400	0.210	0.295
Ethyl disulphide	0.573	0.439	0.278
Iso-amyl disulphide	0.452	0.446	0.454
Tri-methyl thiophene	0.410	0.070	0.103

These data are in fair agreement with the earlier data published by Wood and associates.²⁷

Effect of Treatment.—The treatment with sulphuric acid affects various properties of gasoline, including color, odor, corrosiveness, stability, content of unsaturated hydrocarbons and sulphur compounds. The extent to which the unsaturated hydrocarbons are removed by commercial treatment with sulphuric acid is demonstrated by the data of Morrell,¹⁸ given in Table 161. While the content of aromatic hydrocarbons before and after treatment is practically unchanged, the unsaturates show a decrease after treatment amounting to 3 per cent. The decrease in the content of olefins is greater when larger amounts of acid are employed.

The effect of the relative amounts of sulphuric acid on the various

Table 161. Chemical Composition of Cracked Gasolines Before and After Treatment with Sulphuric Acid.

	—California Cr. Gasoline—		Mid-continent Cr. Gasoline	
	Untreated	Treated With 8 lbs./bbl.	Untreated	Treated With 5 lbs./bbl.
Unsaturates (%)	25.8	23.2	17.8	14.3
Aromatics (%)	10.8	11.5	22.5	21.6

properties of cracked gasolines is shown by the data on California cracked gasolines (Table 162). The data were published by Morrell and Egloff.¹⁹

Table 162. Treatment of California Cracked Gasoline With Sulphuric Acid at Room Temperature.

	0	1½	5	10	15	20	25	30
Acid (lbs./bbl.)		0.30	1.0	2.3	3.4	4.4	5.8	6.7
Acid sol'n loss (%)		0.30	1.0	1.9	2.3	3.2	4.1	4.7
Polymers loss (%)		0.30	1.0	1.9	2.3	3.2	4.1	4.7
Gravity, A.P.I.	50.3	52.5	52.6	52.4	52.3	52.3	52.1	52.2
Color, Saybolt	red	yellow	17	19	22	22	21	20
Gum, (mg./100 cc.) Copper dish	472	232	38	13	6	6	8	7
Sulphur (%)	0.61	0.55	0.48	0.41	0.28	0.25	0.19	0.14
Octane no.	76	74	72.5	72.5	72.0	72.0	71.5	69.5
Induction period (minutes)	600	220	550	All samples cut at 600 minutes.				

The following conclusions may be made on the basis of the data of Table 162.

(1) A marked effect of the treatment is observed with 5 pounds of sulphuric acid per barrel. Smaller charges of sulphuric acid do not appreciably improve the color and stability. It is understood that the effect of the charge of sulphuric acid depends upon the cracked gasoline. In other cases, a satisfactory result with regard to color and stability may be obtained by the use of lesser or greater amounts of the reagent.

(2) The loss in octane number is not large with small amounts of sulphuric acid, but is considerable when 10 pounds of sulphuric acid or more are used per barrel of gasoline.

(3) The removal of sulphur compounds by sulphuric acid is by no means an easy operation. Even the use of 30 pounds of sulphuric acid per barrel reduces the initial content of sulphur 0.61 per cent to 0.14 per cent, *i.e.*, above the accepted specification. A practically complete removal of sulphur compounds may be obtained by the use of an excess of fuming sulphuric acid.

The latest data of Graves^{8b} show that the acid treatment of certain cracked gasolines, mostly highly aromatic, may increase the octane rating due to the removal of constituents whose octane number is below the average. The data of Graves are given in Table 163.

Table 163. Effect of Acid Treatment of Cracked Naphthas on Knock Rating of 400°F. End Point Cracked Gasoline.

Base Stock	None		Acid Rate, lbs. of 98% 10.5		Acid per Barrel, at 20°F. 21.0		31.5	
	Octane No.	Sulphur	Octane No.	Sulphur	Octane No.	Sulphur	Octane No.	Sulphur
Naphtha cracked commercially from:								
So. Calif. res.	70.0	0.62	69.2	0.40	67.8	0.133	66.5	0.062
Kettleman res.	68.1	0.26	66.6	0.095	64.0	0.042	61.3	0.033
Elwood res.	67.2	0.205	65.7	0.067	63.2	0.025	60.5	0.021
Midway gas oil	74.0	0.28	73.2	0.147	72.1	0.056	70.9	0.025
Midway-Huntington Beach res.	71.8	0.70	71.2	0.48	70.5	0.195	69.7	0.087
So. Calif. res.	68.4	0.60	67.4	0.35	66.3	0.122	63.8	0.050
Ingleswood res.	73.6	1.22					73.0*	0.23*
Kern crude	74.1	0.41	74.3	0.26				
Cracked gas. bot.	73.8	0.33			74.5†	0.12†		
Valley gas oil	76.3	0.19	76.8	0.045				
SO ₂ extract	77.3	1.24					79.5†	0.13†

* 35.3 lbs./bbl. † 19.7 lbs./bbl. ‡ 42 lbs./bbl.

The same author shows that the acid treatment, decreasing in general the octane rating of cracked gasolines, invariably increases the response to tetraethyl lead. Thus the octane numbers of the acid-treated cracked

gasolines after leading with 2 or 3 cc. tetraethyl lead are appreciably higher than those of untreated gasolines equally leaded.

Factors of the Treatment.—The principal variables in the sulphuric acid treatment are: relative amount and strength of sulphuric acid, temperature, and contact time. The properties of treated gasolines and the treating losses are affected by these variables.

The effect of the relative amounts of sulphuric acid has been discussed in the previous section. The effect of the strength of sulphuric acid upon the results of the treatment may be compared to a certain degree with the effect of the larger relative amounts of the reagent. Very weak sulphuric acid (less than 60 per cent), however, does not give any effect even when used in large relative amounts. The minimum concentration of sulphuric acid used in commercial practice is from 85 to 90 per cent, if pressure distillates are treated. This concentration may be sufficient for a more or less selective removal of the most unstable unsaturated hydrocarbons. The sulphuric acid commonly used for the treatment of cracked gasolines is the commercial 66°Bé., or 93 per cent acid. The more concentrated 98 per cent acid is employed in the cold treatment process. The refining power of sulphuric acid rapidly increases with increasing concentration up to a concentration of 92-94 per cent, and much more slowly at higher concentrations. The experiments of Kalichevsky and Stagner¹⁴ show a comparatively small difference in the sulphur content of treated gasolines upon the treatment of a cracked gasoline with 93 and 103 per cent sulphuric acid.

According to Retailiau,²¹ a vapor-phase-cracked gasoline may successfully be treated first with diluted sulphuric acid to avoid excessive losses in the treatment. After washing with caustic, it is treated with about 1.4 lbs. per barrel of 30-per cent sulphuric acid. This weak acid removes alcohols (?) and nitrogen bases present in gasoline. In the second stage the cracked distillate is treated with 3 to 17 lbs. of sulphuric acid of a concentration not higher than 90 per cent, preferably 75 per cent. In this stage, the temperature of the treatment is between 125 and 175°F., since the rate of the reaction between dilute sulphuric acid and unsaturated hydrocarbons considerably decreases at lower temperatures. The final product is reported to be satisfactory with regard to stability and color.

The temperature has a very strong effect on the results of the treatment. The rate of the reaction between unsaturated hydrocarbons and sulphuric acid markedly decreases with decreasing temperature, resulting in the reduction of polymerization and losses. On the contrary, the desulphurization of cracked gasolines is favored by the decrease in temperature. The data of Morrell and Egloff¹⁹ illustrate the effect of temperature (Table 164).

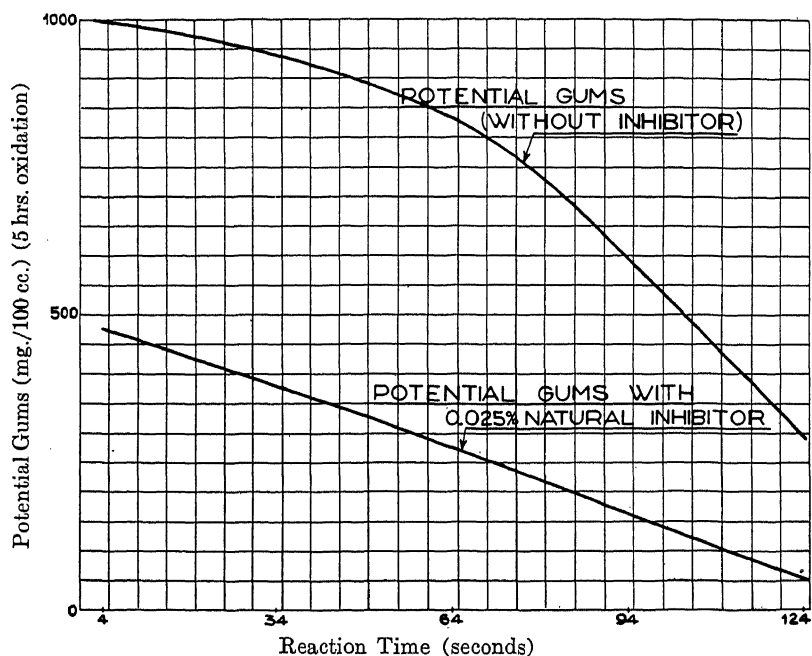
Pierce²⁰ showed that at a temperature exceeding 27°C. (80°F.) gasolines of poor color and containing an appreciable amount of sulphur dioxide were obtained after redistillation. A more complete separation

Table 164. Treatment of California Cracked Distillates with 98 Per Cent Sulphuric Acid at Varying Temperatures.

Temp. (°F.)	Acid, (lbs./bbl.)	% Solution Loss	% Polymers	% Sulphur in Finished Gasoline
100	0	8.1	9.7	0.59
70	30	7.7	6.8	0.13
40	30	7.0	4.9	0.08
18	30	7.5	1.7	0.08
0	30	7.2	1.6	0.07

of water from the cracked distillate is recommended to avoid an increase in temperature during the treatment with sulphuric acid. The rigid temperature control of the treatment within the range of 20 to 60°F. is of primary importance, affecting the losses, the loss in octane number and other results of treatment.^{24a}

Thus the treatment with sulphuric acid should be carried out at moderate or low temperatures. Under these temperature conditions, predominantly the most unstable and objectionable hydrocarbons react

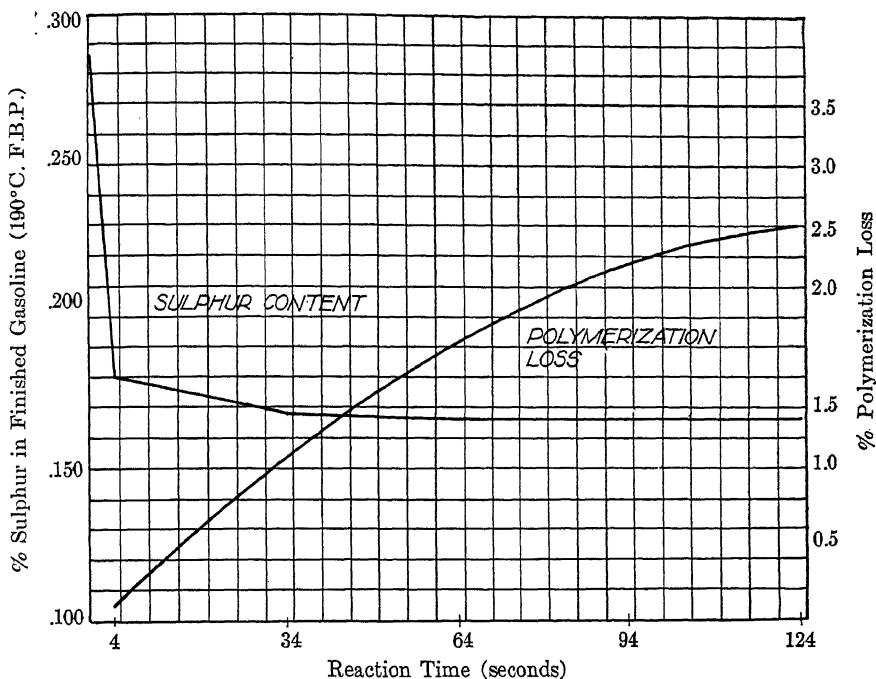


Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 49.—Treatment of Cracked Gasoline with Sulphuric Acid.

with sulphuric acid. As a result, the losses are reduced. On the other hand, treatment under these conditions minimizes the formation of dialkylesters, resulting in a better color and stability of the finished gasoline after redistillation.

The effect of the contact time on the yields and the properties of treated cracked gasolines has been investigated during the last years by many authors. The results of Sager for two Iranian gasolines²⁴ may be summarized in Figures 49-52. Figures 49 and 50 relate to a more unsaturated gasoline of specific gravity 0.732, E.P. 197°C. and a McIlhiney bromine number of 40-50; and Figures 51 and 52 relate to another, more saturated gasoline of specific gravity 0.744, E.P. 208°C., and 30-35



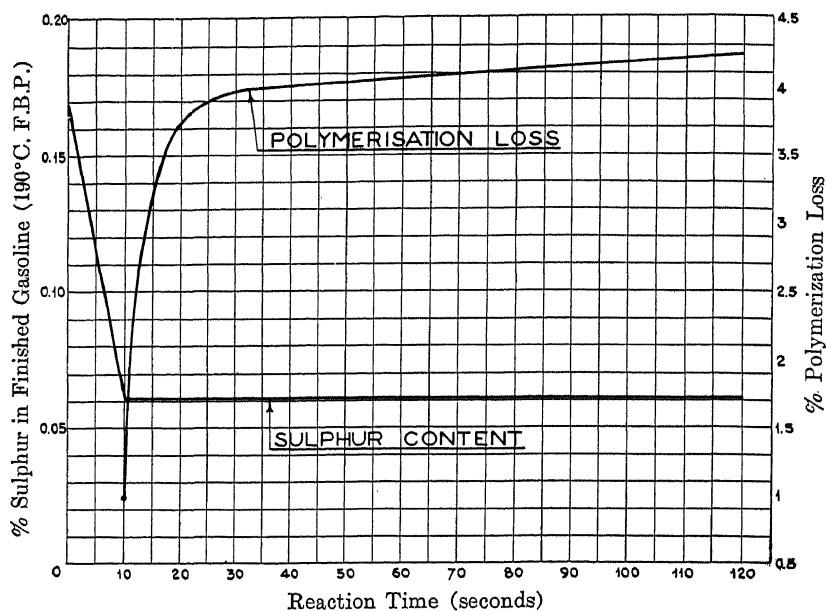
Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 50.—Treatment of Cracked Gasoline with Sulphuric Acid.

bromine number. The relative amount of 96 per cent sulphuric acid employed was 2 per cent, by weight or 6 pounds per barrel.

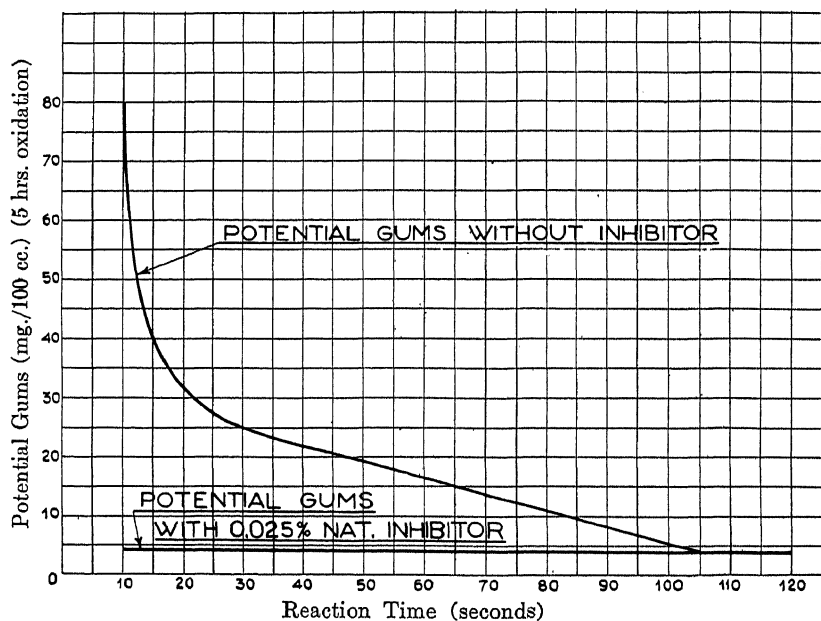
As can be seen from the figures, the time of reaction with sulphur compounds is very short, amounting to 4-10 seconds. After this period of time, equilibrium between the sulphuric acid phase and gasoline phase is attained, and further treatment does not give any noticeable effect. It should be remembered that sulphuric acid has mainly a solvent action on the sulphur compounds present in gasolines. The removal of sulphur compounds in cracked gasolines, investigated by Sager, is comparatively satisfactory, being from 50 to 70 per cent of the original amount.

The reaction between sulphuric acid and unsaturated hydrocarbons is much slower. The time required for appreciable removal of unstable



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 51.—Treatment of Cracked Gasoline with Sulphuric Acid.



Courtesy "Refiner and Natural Gasoline Manufacturer"

FIGURE 52.—Treatment of Cracked Gasoline with Sulphuric Acid.

unsaturates, resulting in a reasonable content of potential gum, is from 30 to 120 seconds. It will be seen from the curves that the time and the extent of the reaction with unsaturates may be considerably shortened by the use of inhibitors.

Thus, according to Sager, the total contact time with sulphuric acid should not exceed from 3 to 10 seconds; the maximum is 60 seconds for desulphurization, and from 80 to 100 seconds and more for the removal of unstable unsaturates and for storage stability. A prolonged time of treatment causes excessive losses of gasoline and favors the formation of diesters of sulphuric acid which are decomposed upon redistillation and impair the color and stability of distilled gasolines.

After treatment with sulphuric acid, the mixture of gasoline and reagent is settled and separated into treated gasoline and sludge. The settling of the acid sludge should be effected as rapidly as possible. A prolonged settling period produces the same negative results as are caused by a prolonged treatment. Washing with water and neutralization follow the settling.

The consumption of 66°Bé. sulphuric acid in the treatment of cracked gasoline varies between 1 and 5 lbs. per barrel to obtain satisfactory color and gum stability. The removal of sulphur compounds is very incomplete under these conditions, usually not exceeding 50 per cent of the original content of sulphur. Much larger quantities of sulphuric acid are required for further reduction of the sulphur content. The caustic soda used for neutralization may be of 2 to 15°Bé., on an average, about 6°Bé.

The treating losses average about 3 per cent for 5 lbs. of sulphuric acid per barrel and 5 per cent for 10 lbs. per barrel. The losses include those in acid sludge and in polymerization.

The average cost of the treatment of mixed-phase-cracked gasoline with sulphuric acid is about 4 cents per barrel, including the losses. It is assumed that the treatment does not involve desulphurization of the gasoline.

In a few refineries treatment with fuller's earth is substituted for neutralization. The cracked gasoline is filtered through fuller's earth after the acid treatment without neutralization. Redistillation follows the filtration.

In some cases, when the quantity of sulphuric acid used is very small, about 1 lb. per barrel, the treatment with floridin (about 2 lbs. per barrel) may be employed without subsequent redistillation.

Commercial Treating Plants.—Continuous treatment has many advantages over batch treating. The mixing of the gasoline under treatment with the reagent is effected in columns of small diameter, the reagent and the product being both charged to the lower part of the column. The column is equipped with a varying number of orifice plates, or it may be equipped with baffles. The orifice columns are more effi-

cient. The flow of the liquids through orifices is turbulent, producing intimate mixing of the gasoline and acid.

Settling of the treated product from the sludge is carried out in tanks, either in the horizontal or, more frequently, in the vertical type. The diameter of the tank selected is of such size as to permit a given amount of the liquid to remain in this apparatus from one to two hours. Sometimes additional special tanks, dislodgers, charged with coarse sand, gravel, etc., are used for a better separation of the sludge.

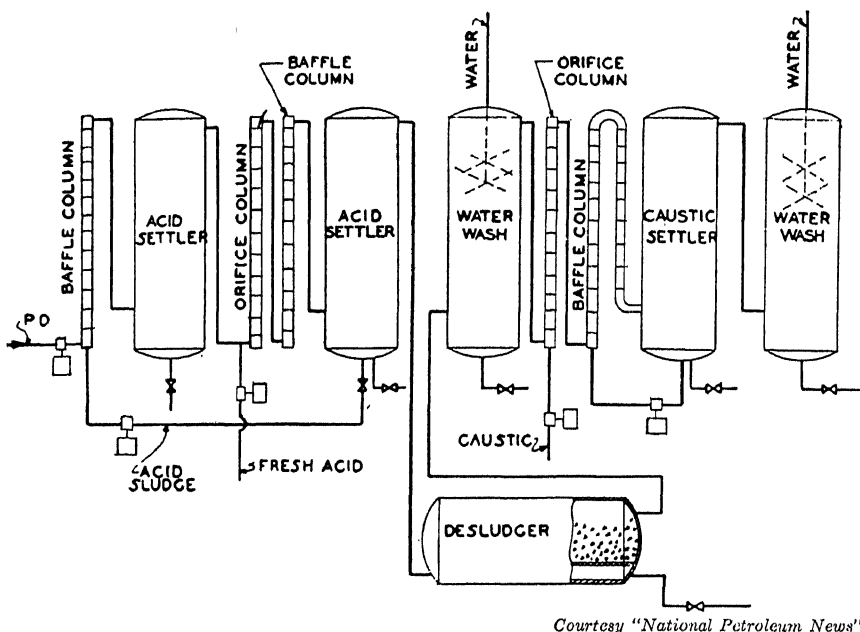


FIGURE 53.—Sulphuric Acid Treating Process.

The layout in Figure 53 shows a continuous acid and alkali treating plant. The pressure distillate (P.D.) is pumped into the first mixer together with the spent acid. This preliminary treatment is followed by settling in a tank. The second mixer is charged with fresh acid, this operation being followed by a second settling in a tank. The final settling from the acid sludge is effected in the deslugger. The product finally passes into a tank where it is sprayed with water. The distillate then passes into a third mixer which is charged with caustic. The caustic may be either fresh or taken from the following tank. From the third mixer the product is passed into a settling tank and it is finally sprayed with water in a succeeding tank.

Thus separation of the reagents from the product is effected by direct gravity settling. The use of centrifugal separators is much more effective. During recent years, centrifugal separators have been used more

extensively in the treatment with sulphuric acid. In using the centrifuges, the mixing of the gasoline and sulphuric acid is performed in special efficient contactors for a short time, not exceeding 3-60 seconds. Separation is effected by passing the mixture of acid and gasoline through a centrifuge, the settling tanks being eliminated; separation in centrifuges also requires a short period of time, about 1-2 seconds.

There are three different acid treating processes using centrifuges: DeLaval, Stratford and Sharples. The process is carried out in one, two or three stages. The Stratford process uses a low temperature. Figure 54 represents the flow diagram of the Stratford process using three stages.

Low-Temperature Treatment.—As has been previously mentioned, the losses of the product treated are very high when the amount of sulphuric acid exceeds 15 lbs. per barrel of cracked distillate. In addition to this the octane numbers of finished gasolines are impaired. Even under these rather severe conditions of treatment, the removal of sulphur is incomplete. A prohibitive consumption of sulphuric acid, involving enormous losses, is frequently required to meet the specification 0.1 per cent of sulphur in the finished gasoline.

The low-temperature treatment has been developed mainly for California cracked gasolines with high sulphur content. At the low temperatures of -9 to -12°C . (20 to 15°F .), sulphuric acid retains its activity as a solvent for sulphur compounds, but loses most of its reactivity with unsaturated hydrocarbons. Thus under these temperature conditions, relatively large proportions of sulphuric acid may be used without an excessive reaction with unsaturated hydrocarbons and without excessive losses. Due to the limited extent of its reaction with unsaturates, the acid is not diluted with the products of the reaction, thus retaining its solvent power. On the other hand, the strength of sulphuric acid is sufficient to remove the most unstable unsaturates even at a low temperature. As a result, the stability of treated gasolines is satisfactory. The octane number is impaired to a much less extent than at higher temperatures of the treatment.

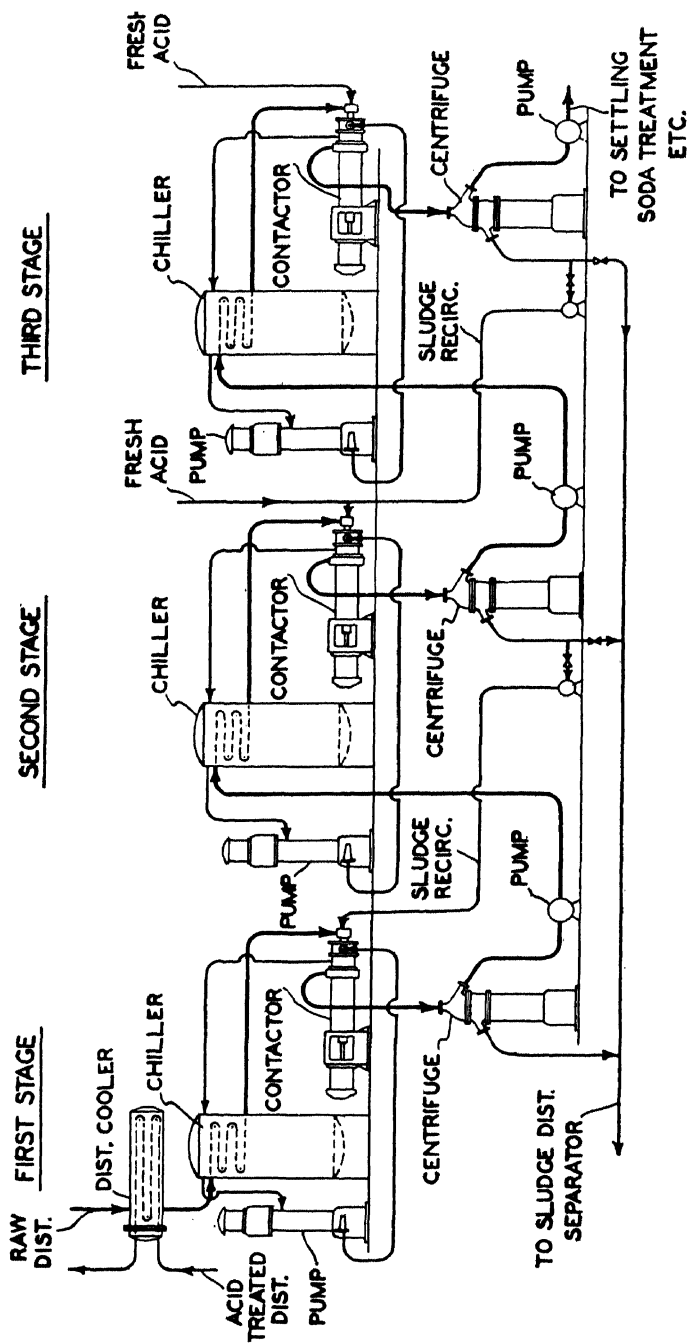
The consumption of sulphuric acid and yields of finished gasoline at various temperatures of the treatment are given by Halloran⁹ and summarized in Table 165.

Table 165. Treatment of California Cracked Naphtha* at Various Temperatures to Produce Gasoline of U.S.M.G. Boiling Points.

Maximal temperature of treatment ($^{\circ}\text{F}$.)	5	20	30	45	60	100	166
Lbs. of 98% acid per gal. of naphtha	0.60	0.51	0.60	0.63	0.84	1.15	1.50
% sulphur in treated gasoline	0.27	0.38	0.36	0.49	0.58	0.74	0.79
Polymerization loss	4.6	2.7	6.9	9.6	14.2	20.5	33.1
Acid treatment yield	92.7	92.7	92.8	91.8	90.2	88.3	78.9
Rerun yield	88.7	90.5	86.6	84.1	79.8	74.0	62.2

* Naphtha of 53.7 A.P.I. Gravity, Per Cent of Sulphur 0.71, Per Cent of U.S.M.G. 93.0.

The figures of Table 165 clearly show the gain in the yields of finished gasoline and in the consumption of sulphuric acid at low temperatures. The best results were obtained at 20°F . At still lower temperatures the



Courtesy "Oil and Gas Journal"

FIGURE 54.—Centrifuge Sulphuric Acid Treating Process.

viscosity of the sludge becomes very high, impairing the results of treatment.

The scheme of the low-temperature plant does not differ essentially from that of the conventional countercurrent process. The commercial plant of the Standard Oil Company of California uses a treatment in three stages. The naphtha passes through a cool exchanger and a series of coolers. The temperature of the naphtha in the outlet is from 0 to 10°F. After the first treatment, the mixture of sludge and naphtha is discharged into the first sludge settler. The separated naphtha is again cooled to 10-15°F. and then treated in the second stage. After the second separation in the appropriate settler, the naphtha is finally cooled again to 10-15°F. before the third stage of the treatment. Other operations are conventional. Only strong 98-per cent sulphuric acid is employed in the low-temperature treatment. It is understood that the refrigeration of products involves high additional operating expenses.

Redistillation

The treatment with sulphuric acid and neutralization are followed by redistillation to remove polymers and dialkylesters of sulphuric acid formed in the treating process and dissolved in the treated gasoline or naphtha. Redistillation is carried out under very mild temperature conditions to prevent decomposition of unstable dialkylesters to sulphur dioxide. Disulphides may also be partially decomposed. As a result of the decomposition, the stability and color of the finished gasolines would be impaired. Thus distillation in pipe stills is preferable to distillation methods where shell stills are used and where the product is necessarily exposed to high temperatures for a prolonged time.

Distillation in a single shell still is nevertheless carried out in small refineries quite frequently. The temperature of distillation ranges from 160°C. (320°F.) to 220°C. (430°F.) with a steam consumption of 350 lbs. of steam per barrel of pressure distillate in the first case and 50 lbs. in the second case.

In a pipe still the pressure distillate is heated up to 180-200°C. (356 to 392°F.) and passes then into a bubble tower for fractionation. Steam is introduced, as usual, in the bottom of the column. Here a great saving in steam is effected, only from 10 to 30 lbs. being required per barrel. On the other hand, the time of heating in the pipe still is short, minimizing the decomposition of dialkylesters and disulphides. Experiments carried out by Pierce²⁰ showed that, other conditions being equal, the amount of steam used determines the amount of free acid present in the distilled gasoline. It should be kept in mind that this free acid comes from the decomposed dialkylesters of sulphuric acid.

In many cases satisfactory results cannot be obtained by temperature adjustment and the introduction of steam. The distilled gasoline contains a noticeable amount of free acid and its color is unsatisfactory. Sodium carbonate or soap amounting to about one pound per barrel of petroleum

distillate must be introduced during distillation. This method of distillation usually produces very good results. The gasoline obtained is neutral, stable and has a good color. It is possible, when introducing caustic, to materially raise the heating temperature of the distillate to 220°C. (430°F.) and to lower the steam consumption materially.

Still better results are obtained in vacuum distillation in which the temperature of distillation is considerably lower. The process is carried out in two stages. In the first heater the pressure distillate is heated to 125-135°C. (257-275°F.) under atmospheric pressure. From the atmospheric heater the charge is flashed into a fractionating tower, producing light gasoline and residuum which is pumped to the second heater under vacuum. The residuum, heated to the same temperature 125-135°C. (257-275°F.) in the second heater, passes to a second fractionating tower under reduced pressure of about 100 mm. In the vacuum tower a heavier distillate is separated from pressure distillate bottoms.

Since the temperature of redistillation in both stages of the vacuum process is low, the use of the conventional furnaces with direct heating is unnecessary. The charging stock, preheated in heat exchangers, enters the special evaporator, heated indirectly by steam, which transfers its latent heat of condensation to the gasoline. The hot water condensed returns to the boiler. By this method any local overheating of the charging stock is completely eliminated.

As has been mentioned above, redistillation of treated pressure distillates is followed by the final doctor treatment.

The average cost of the conventional redistillation is about 2 cents per barrel, including the losses and degradation (polymerization). The total average cost of the treatment with sulphuric acid, rerunning and sweetening is about 6-7 cents per barrel including losses and degradation. It is assumed that the treatment does not involve desulphurization of the gasoline treated.

The Zinc Chloride Process

This process, developed by Lachman,¹⁶ uses a concentrated aqueous solution of zinc chloride for the treatment of cracked gasolines. The reaction takes place in a tower filled with suitable packing or provided with baffles (Figure 55). The vapors of the gasoline to be refined pass into the tower, meeting a continuous flow of zinc chloride solution. The temperature of the process ranges between 150 and 175°C. (302-347°F.). The time of contact between the vapors and the solution is very short, usually 2 seconds; 12 seconds is the longest time that has been used. The concentration of zinc chloride in the solution varies from 70 to 85 per cent by weight. The relative amount of zinc chloride solution per barrel of distillate being treated varies from 1 to 10 lbs. Hydrogen chloride formed during the treatment is neutralized with ammonia injected before the bubble tower. Partial neutralization of the vapors takes place in the

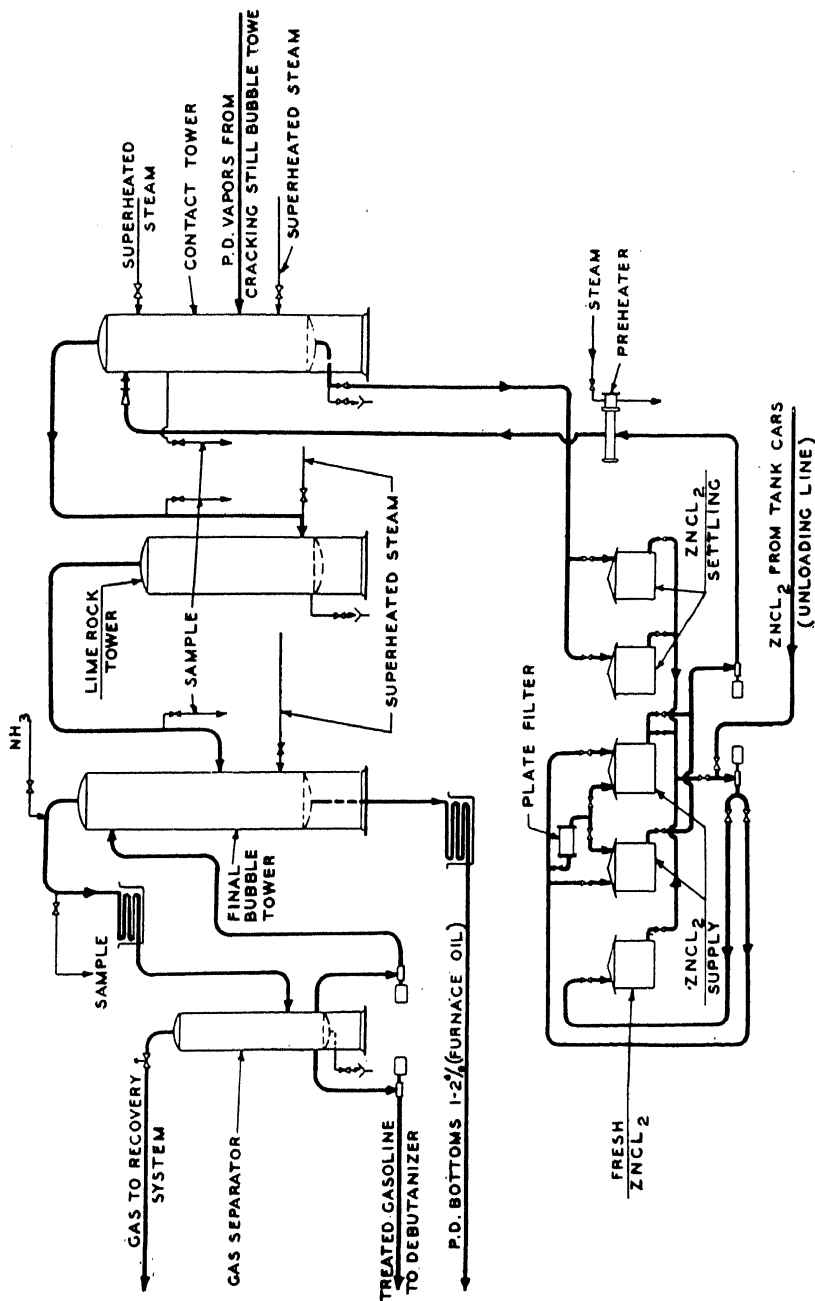


FIGURE 55.—Lachman Treating Process.

Courtesy "Oil and Gas Journal"

rock lime tower from which the vapors pass into the bubble tower for final distillation.

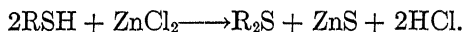
The losses on the treatment are reported to be very small, only 0.23 per cent for a commercial run. The properties of a raw and a treated gasoline are as follows:

	Raw	Treated and Redistilled
A.P.I. Gravity	53.2	55.9
Gum (copper dish) (mgs.)	290	3
Sulphur (%)	0.28	0.19
Mercaptans, as molar	0.017	0.007
Color, Saybolt		30

The average reduction in sulphur is from 25 to 40 per cent.

The treatment does not affect the octane numbers. The consumption of zinc chloride amounts from 0.1 to 0.3 lb. per barrel of gasoline. The recovery of the spent solution of zinc chloride is simple. The discharged solution is diluted with water to a concentration of about 50 per cent and settled. A great part of the zinc chloride is recovered in the solution formed. Zinc chloride in this treatment may be replaced by many other chlorides of heavy metals.

Little is known of the chemistry of the Lachman process. The action of zinc chloride on unstable unsaturated hydrocarbons is probably catalytic. Unstable unsaturates, such as diolefins, are selectively polymerized, while olefins are not affected. According to Lachman, mercaptans may react with zinc chloride as follows:



This reaction is responsible for the partial removal of sulphur. In addition to it, a certain condensing action of zinc chloride upon sulphur compounds has been observed, resulting in increase in the boiling point of sulphur compounds after the treatment.

The cost of the zinc chloride treatment is claimed to be \$0.0582 per barrel treated, the cost of sweetening not being included in this figure.

A modification of the Lachman process is used in Russia.²⁵ Pumice (in lumps from 2 to 10 mm. in size) is impregnated with a 30°Bé. solution of zinc chloride and then dried by flue gases at a temperature not exceeding 220-240°C. The control of the temperature of drying is very important, since the efficiency of the catalyst is impaired at higher temperatures.

The content of zinc chloride in pumice is about 10-12 per cent by weight with respect to pumice. The pumice covered with zinc chloride is charged into a treating column. The vapors of a cracked distillate at a temperature of 200 to 220°C. pass upward through the column forming polymers and products of condensation. The working cycle is approximately 15 days. The consumption of zinc chloride is reported as 0.2 per cent by weight with regard to the charge.

Treatment of cracked gasolines with aluminum chloride gives very satisfactory results with respect to stability. In addition, the desulphuriz-

ing action of aluminum chloride is much stronger than that of zinc chloride. The treatment with aluminum chloride is performed at low temperatures, about 20°C. or somewhat higher. The quantity of aluminum chloride can be limited to 0.5 per cent by weight, but the reagent spent cannot be regenerated.

The Howard Process

This process using chlorine and zinc chloride has been described by Kaye.¹⁵ The stabilized gasoline is vaporized in a stripping column, where an undisclosed amount of free chlorine is added. The vapors pass into the lower part of a contact tower filled with oxidized zinc (zinc oxide or zinc oxychloride) dispersed through the tower in a solid binder. After passing through the contact tower, the vapors are fractionated in the second fractionating tower and the overhead distillate is the finished gasoline. The polymers from the second fractionating tower and the contact tower are fed into the first stripping column and are withdrawn. The yields of polymers are not disclosed. The process sweetens gasoline, and further sweetening is not required. The process not only improves the color, odor and gum-forming properties of cracked gasolines, but removes part of the sulphur, bound in mercaptans. The octane numbers are not attacked, nor is lead susceptibility decreased. The data of Table 166 are illustrative of the process.

Table 166. Treatment of Cracked Gasolines by the Howard Process.

	P.D. from Michigan Crude		P.D. from Coastal Crude		Reformed P.D.	
	Raw	Treated	Raw	Treated	Raw	Treated
Gravity, A.P.I.	61.6	61.3	55.0	54.6	51.1	51.7
Color, Saybolt	Lt. Yel.	30+	orange	30+		30+
I.B.P. (°F.)	80	88	76	82	112	104
10 per cent (°F.)	124	130	137	138	202	190
90 per cent (°F.)	350	355	361	354	415	392
E.P. (°F.)	381	404	375	388	458	418
Copper dish gum (mgs.)	85	3.3	191	14		
Induction period (min.)	115	400+	145	400+		
Total sulphur (%)	0.0467	0.024	0.063	0.042	0.0214	0.011
Mercaptan sulphur (%)	0.0250	0.000	0.017	0.000		
Octane no.					59.0	59.9
T.E. Lead to 70 O.N. (cc.)					1.8	1.8

The consumption of chlorine is between 0.05 and 0.25 lb. per barrel. The contact mass can be periodically reactivated by steaming.

Clay Treating Processes

The treatment of crude gasolines by the action of fuller's earth is widely used in the United States and abroad. According to Mandelbaum and Swanson,¹⁷ the total daily capacity of all clay treating installations was 221,600 barrels in 1937. The distribution through different countries and processes is given in Table 167.

The Gray Process.—It is known that the hydrocarbons are selectively absorbed by fuller's earth in increasing order from paraffins to aromatics and unsaturates. For the unsaturates with two double bonds, the adsorption is followed by condensation or polymerization which may

Table 167.

	U. S.	Other Countries	Total
Gray	150,000	25,000	175,000
Stratford	16,000	600	16,600
Osterstrom		30,000	30,000
Total	166,000	55,600	221,600

occur even at low temperatures. For instance, turpentine is readily polymerized in the presence of floridin at room temperature, the process being accompanied by a strong evolution of heat. At elevated temperatures, used in commercial treatment of cracked gasolines up to 246°C. (475°F.) and higher, the adsorption of hydrocarbons by clay is of secondary importance, but polymerization reactions of diolefins and similar unstable unsaturates readily take place, transforming the hydrocarbons into gum.

The action of fuller's earth on cracked gasoline is different from that of sulphuric acid. While the latter reacts strongly with the aromatic and unsaturated hydrocarbons, sulphur compounds and resinous substances, the action of fuller's earth is considerably more moderate and selective. Fuller's earth condenses mainly diolefins, converting them into heavier products of polymerization without attacking the aromatics and olefins. The advantage of fuller's earth over sulphuric acid lies in the fact that the valuable compounds of the cracked gasoline remain unchanged; the losses on treatment with fuller's earth are therefore much lower than those in sulphuric acid treatment. The disadvantage of the fuller's earth treatment is that it does not react with sulphur compounds. Treatment of cracked gasoline with fuller's earth produces the following results:

(1) The composition of the gasoline does not change after the treatment. The specific gravity of the treated gasoline is higher by 0.002 to 0.003 than before treatment.

(2) The color improves as a rule after treatment and always becomes more stable.

(3) The amount absorbed by sulphuric acid does not change after the treatment. The iodine number decreases by 2 to 10 per cent.

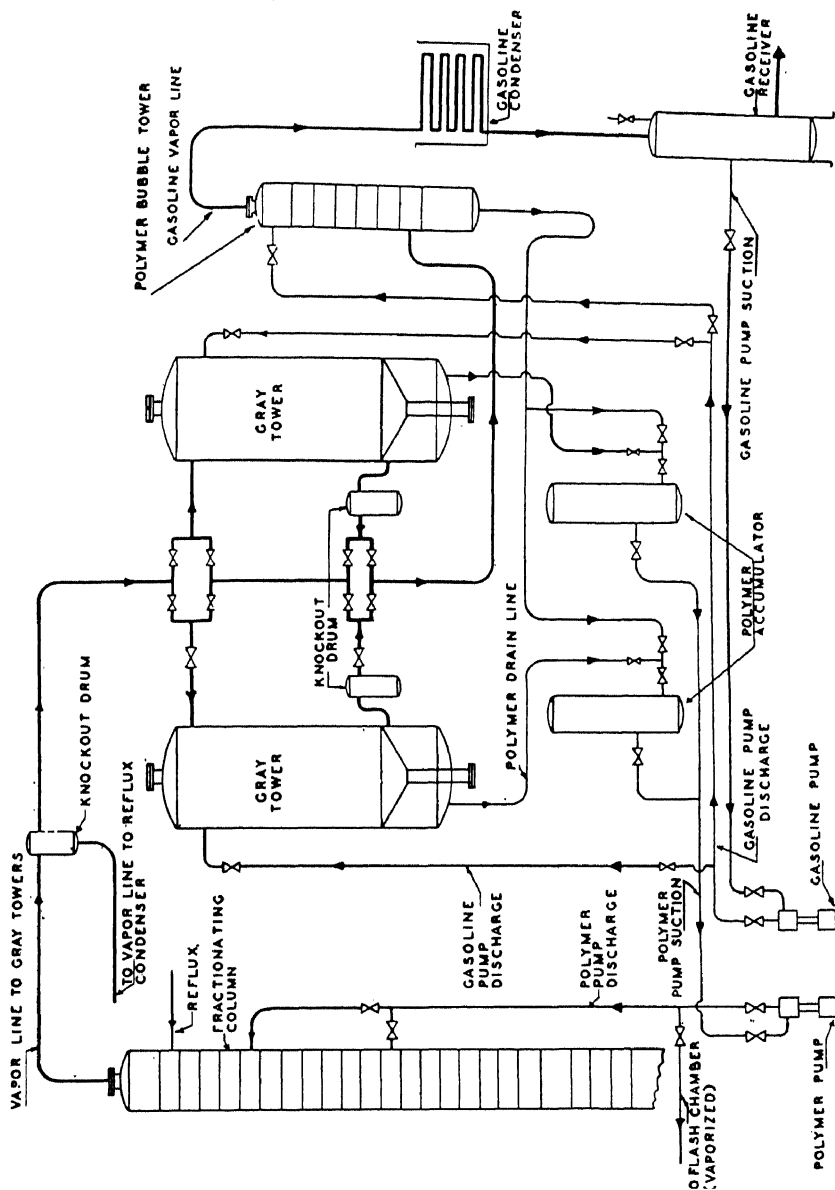
(4) The amount of sulphur in the gasoline does not change after treatment.

The first and most widely used method is the Gray process in which vapors of cracked gasolines pass through a bed of fuller's earth. Figure 56 is a flow sheet of the Gray process with two treating towers which are in alternate operation. The towers are directly connected with the fractionating column of the cracking unit. The polymers or condensates formed contain a considerable proportion of gasoline and are conveyed either to the above fractionating column or to the flash chamber for stripping. The total amount of true polymers, stripped from gasoline, formed in the Gray process from mixed-phase-cracked gasolines does not exceed 1 per cent.

The improvement in gum formation, color and color stability in the Gray process depends on the contact time. As a rule, cracked gasolines from paraffinic stocks, from distillates or produced under mild conditions

FIGURE 56.—
Gray Treating
Process.

Courtesy "Oil and
Gas Journal"



of cracking are treated more easily by the Gray process than those produced from residual stocks, or cracked under severe cracking conditions.

The following data concerning the Gray towers are to be mentioned:

Capacity	80 to 12,000 bbls./day
Diameter (feet)	5 to 25
Depth of clay bed (feet)	6 to 25
Time of contact (seconds)	20 to 400
Temperature (°C.)	121 to 246
Temperature (°F.)	250 to 475
Pressure (lbs./sq. inch.)	5 to 380, usually 50-100
Pressure drop (lbs./sq. inch)	2 to 50
Throughput	800 to 27,000 bbls./day

As soon as the activity of fuller's earth is decreased to a noticeable degree, the tower is shut off by means of special valves and live steam is passed through the lines indicated in the drawing to drive off the gasoline vapors. As soon as the vapors are all drawn off the fuller's earth is discharged through the lower manhole. Under normal conditions the fuller's earth is changed once to four times a month, depending on the quality of the gasoline.

The relative amount of fuller's earth used varies within very wide limits, depending on the quality of the gasoline treated and on the pressure. One ton of fuller's earth at a pressure of 40 to 60 pounds per sq. inch treats a minimum of 2000 barrels, which corresponds to about 0.5 per cent of fuller's earth calculated on the gasoline. When higher pressures are used (150 to 200 pounds per sq. inch), a higher yield of gasoline per ton of clay—about 4000 barrels—may be expected. Cases are known where from 8000 to 15,000 barrels of gasoline were treated with a ton of fuller's earth. If inhibitors are used in finished gasolines (clay-treated and sweetened), the throughput can be greatly increased. In such cases the clay treatment removes only highly unstable hydrocarbons.

The initial cost of the Gray towers is about \$20 per barrel of daily capacity. The cost of treating cracked gasolines with fuller's earth by the Gray process amounts to \$0.023 per barrel, omitting royalties and sweetening costs. At any rate the treatment with fuller's earth is considerably cheaper than that with sulphuric acid.

The comparative cheapness of the fuller's earth treatment in the vapor phase is due to the elimination of redistillation after treatment, to small losses, and to the small amount of the reagent used. The gasoline from the Gray tower contains in many cases sulphurous acid which is removed by washing with a solution of soda. Treatment with the doctor solution is required to obtain a negative doctor test.

The polymers formed in the Gray process are liquid, but exposed to air they gradually harden to a solid gum. The specific gravity of polymers is about 0.800 to 0.825 and the boiling range from 85 to 288°C. (185-550°F.). The clays successfully used for the Gray processes are Attapulgis, Floridin, Olmstead earth and Riverside (Texas). The following data of Cooke and Hayford⁷ illustrate the results of the Gray process (Table 168).

Table 168. Effect of Clay Treating on Color, Gum and Octane Number of Cracked Gasolines.

Cracked Gasoline from	—Before Gray Treatment—					—After Gray Treatment—				
	A.P.I. Gr.	E.P. (°F.)	Color	Copper Dish Gum	O.N.	A.P.I. Gr.	E.P. (°F.)	Color	Copper Dish Gum	O.N.
Top. colon	51.1	392	off	57.5	57.5	59.1	366	30+	6.5	68.5
Top. Western	56.5	390	off	160.0	75.0	56.6	386	30+	0.7	75.0
Midcontinent	50.8	437	off	510.0	67.5	51.0	434	27+	11.0	68.0
Kansas	52.0	437	off	480.0	65.0	52.3	436	28+	11.0	65.0
Reformed	52.8	428	off	179.0	55.0	52.7	424	30+	2.5	54.0
M.C. vapor-phase	47.8	438	off	1177.0	85.0	47.9	440	30+	52.0	83.0
Mirando	50.6	416	off	248	82.0	50.2	417	30+	6.0	81.0
Top E. Texas	56.8	426	off	203	62.0	55.9	427	30+	6.0	62.0
Refugio	48.6	423	off	273	69.0	48.4	422	30+	4.5	69.0

These data show that the color and gum formation of treated gasolines are considerably improved, while A.P.I. gravity, end point and octane numbers are practically unaffected.

The preferred application of the Gray process is in direct combination with the bubble tower of the cracking unit. Such an arrangement eliminates repeated distillation of gasolines.

The Osterstrom Process.—The Osterstrom liquid-phase clay treating process uses a higher temperature of treatment, between 288 and 343°C. (550 and 650°F.). The process, being performed under high pressures of 500 to 1000 lbs./sq. inch gauge, is substantially a liquid-phase operation; it has been described by Holland¹¹ and Cooke and Hayford.⁷

The Osterstrom process was developed for the Gyro vapor-phase-cracked gasolines, which require more severe conditions of treatment due to the higher content of unsaturated hydrocarbons, particularly diolefins. On the other hand, the Gyro vapor-phase-cracked gasolines cannot be successfully treated in the conventional Gray towers connected directly with cracking units because of the large amount of highly reactive olefinic gases produced in the process. The gases are polymerized in the presence of clay, and the clay rapidly loses its polymerizing power.

In the first Osterstrom units, cracked gasoline and clay were mixed and pumped together through a pipe still. In further development, the Osterstrom process becomes similar to the Gray process, being conducted, however, in the liquid phase. Fuller's earth (30-90 mesh) is charged into a special chamber adapted for high pressures. The pressure distillate is pumped through heat exchangers and further to the convection and radiant sections of a conventional pipe still. The high pressure used holds the distillate substantially in the liquid phase. From the pipe still the distillate passes into the clay chamber, the high pressure being maintained. The pressure is released between the clay tower and bubble tower, where the distillate is fractionated to the end point specified.

The following data represent the operation of the Osterstrom process (Table 169).

Since the gasoline went into a dyed motor fuel, no attempt was made to obtain 25+ color. The octane numbers of gasolines before and after treatment are practically the same, provided the end point is unchanged.

Table 169. High-pressure Clay Treatment of Gyro Distillate from M.C. and Michigan Reduced Crudes.

Operating Data:											
Throughput (bbls./day)								2500-4000			
Pressure (lbs./sq. inch)								1000			
Temperature, tube still out (°F.)								550-580			
Temperature, Clay chamber out (°F.)								580-630*			
Total Charge (bbls.)								166,342†			
Clay yield (bbls. of finished gasoline per ton of clay)								71,942			
-----Quality of Products-----											
	Gravity							% at			In-
	A.P.I.	I.B.P.	10%	20%	50%	90%	E.P.	500°F.	Color	Gum	duc-
Charging stock	54.4	87	136	165	263	387	435				tion
Finished gyro	54.7	90	129	166	265	393	417		16-22	2	Per-
Polymers	23.9	416	438	448				49			iod

* The reaction between the clay and gasoline is accompanied by the evolution of heat which is responsible for the increase in temperature in the chamber.

† One charge of clay was used for approximately 4½ months.

A very high yield of finished gasoline per ton of clay over 70,000 barrels is very significant and rather unexpected.

The Stratford Process.—The Stratford slurry clay method described by Cooke and Hayford,⁷ has been developed by Imperial Oil Refineries, Ltd., Canada. In contradistinction to the Gray and Osterstrom methods, this method provides counter-current treatment of gasoline vapors with clay. Conventional bubble towers can be adapted for the treatment, provisions being made for charging fine clay in the form of slurry to the top plate and withdrawing the spent clay from the bottom plate.

The slurry is made in the tanks by mixing heavy straight-run naphtha with 100-mesh clay. The amount of clay used is approximately 2 lbs. per barrel of gasoline. The slurry is pumped to the top of the treating tower. The gasoline vapors to be treated are introduced at the bottom of the treating towers and passed counter-currently to the descending slurry. The slurry passes out of the bottom of the treating towers into a cone settling tank. The liquid, formed in the top of the cone settling tank, is pumped out. The slurry from the bottom of the cone passes into a collecting chamber underneath, where it is completely dried.

The results of the operation are given in Table 170. It should be explained that the pressure distillate from Tube and Tank units is charged to the rerun batteries. Each battery consisting of two stills receives about 200 barrels of pressure distillate per hour. The first still operates at about 360°F. and discharges to the second, which operates at 440-450°F. The gasoline is divided into two approximately equal streams of light and heavy. Each stream is treated separately in two treating towers.

The Houdry Process.—The Houdry process for the treatment of cracked gasolines¹² involves more severe conditions than the Gray and other processes described above. The vaporized gasoline at a temperature of about 315°C. (600°F.), under pressures of 15 to 100 lbs. per sq. inch gauge, passes through a catalytic chamber containing a molded solid

Table 170. Summary of Stratford Clay Treating Operations.

Charged to Battery per hours (bbls.)	200-225
Still temperature:	
Light (°F.)	325
Heavy (°F.)	440-450
Bubble tower, top	
Light (°F.)	250
Heavy (°F.)	330
Clay tower, top	
Light (°F.)	230-240
Heavy (°F.)	310-330

Properties	Charge to Stills	Blended Finished Product
Gravity (A.P.I.)	55.1	58.8
E.P. (°F.)	488	402
Color, Saybolt		29
Gum, porcelain dish (mgs.)		5-8
Sulphur (%)	0.082	0.057
Acid heat (°F.)		13

catalyst. The catalyst consists of activated clay, including oxides of the heavy metals, such as manganese and nickel. Houdry described¹³ the refining of gasolines in two stages. The first stage is carried out in a desulphurizing zone containing a relatively inert adsorbent impregnated with nickel, cobalt or copper oxides. The temperature in this zone is within the range 300-400°C. (572-752°F.). From the desulphurizing zone the product passes into a refining zone containing a catalyst comprising a blend of silica and alumina with a relatively small proportion of nickel, cobalt or copper. The temperature in the second zone is maintained below the temperature of the desulphurizing zone and above 200°C. (392°F.).

The usual operating period lasts from four to six hours, after which the catalyst loses its original activity. Regeneration takes place *in situ* by air at moderate temperatures. Two treating chambers are used for the continuous operation.

In contradistinction to the Gray process, the Houdry process completely removes mercaptans (and hydrogen sulphide) and at least 30 per cent of the original total sulphur. The stability of the gasoline is markedly improved. The yield of treated gasolines is about 96-97 per cent with reference to the raw product.

A stronger effect of the Houdry treatment in comparison with the Gray process is evidently due to a higher temperature used, as well as to the presence of heavy metals which decompose the sulphur compounds of gasolines.

A similar process described by Foster^{8a} uses bauxite as a catalyst. The temperature of the treatment is about 400°C. (750°F.), and the pressure about 15 lbs. per sq. inch. The flow rate in one case is given as 255 barrels per ton of catalyst per day. As a result of the treatment, the distillation range of the treated naphtha is almost unchanged and the

octane number increases by only 3-4 units. However the desulphurization is very complete, the content of sulphur decreasing from 0.425 to 0.011 per cent, or from 0.143 to 0.005 per cent. Desulphurization enhances very appreciably the response to tetraethyl lead and thus causes a considerable saving, for instance, in one case a decrease from 1.74 cc. to 1.00 cc. of tetraethyl lead to produce 73 octane number fuel.

The above results relate to straight-run gasolines. Cracked gasolines give less satisfactory results with respect to desulphurization and require higher temperatures involving high losses. Desulphurization of gasolines by hydrogenation has been described in Chapter 3 (p. 222).

The new desulphurization methods substantially differ from the conventional sulphuric acid treatment, in which the sulphur reduction is performed to meet sulphur specifications of the gasoline. The new desulphurization methods reduce the sulphur content of gasolines to very minute amounts in order to take advantage of the increase in lead susceptibility and of the decrease in lead consumption.

Treatment with Solvents

The solvent refining of cracked gasolines not being used so far commercially, should be discussed as a possible trend in the further development of the treatment of cracked gasolines. It is known that aromatics are very soluble in commercial solvents, being followed by olefins. Naphthenes and paraffins have a minimum solubility in solvents. Thus by the solvent treatment cracked gasolines can be separated either into aromatic-olefinic and naphthenic-paraffinic portions or into aromatic and olefinic-naphthenic-paraffinic portions depending upon the conditions of the treatment.

The data on the treatment of various straight-run gasolines have been published by Saegbarth, Broggin and Steffen.²³ Sulphur dioxide was employed as a solvent at low temperatures of the operation from 0 to -60°F . The amount of sulphur dioxide used was from 40 to 85 per cent by volume. At lower temperatures of extraction, the products obtained consisted predominantly of aromatics, A.P.I. gravity being 32-34, Kauri-butanol number 82-88, octane number (A.S.T.M. Motor method) 89-91, content of aromatics about 85 per cent. The yields, depending upon the gasoline, varied from 10 to 33 per cent of the original. The raffinates produced after the removal of the extracts were highly paraffinic, containing 72-82 per cent of paraffins. As a result, the octane numbers of the extracts were poor, below 41. The solvent treatment of straight-run gasolines is reported to be in commercial operation.

The following results on the solvent treatment of a cracked gasoline were reported by Defize.⁸ A Dubbs pressure naphtha from Borneo crude oil was treated with 300 per cent sulphur dioxide at -10°C . in a batch operation. The results of the treatment are given in Table 171.

The solvent treatment of cracked gasolines cannot be made parallel

Table 171. Solvent Treatment of Cracked Naphtha.

	Cracked Naphtha	Raffinate	Extract
Sp. Gr. at 15°C.	0.804	0.783	0.846
A.S.T.M. Distillation (°C.)			
I.B.P.	125	156	120
10%	180	182	177.5
50%	192	195	195
90%	207	201.5	202
E.P.	208	209	210
Aromatics (% by wt.)	41.3	28.3	65.1
Sp. Gr. of aromatic-free	0.788	0.720	0.778
Yield (% by wt.)		64.5	35.5

to the conventional methods of treatment discussed above. It separates a cracked gasoline into two products of different chemical composition and different properties. The raffinate is a very poor motor fuel due to a low octane number. Thus the method in question cannot be considered as one of the methods of refining motor fuels. Although the extract is of high octane value, the use of it as a blending material for motor fuels does not appear to be particularly promising. It should be emphasized that the octane number of the blended fuel would be close to that of the original cracked gasoline, if a reasonable amount of the extract is used. The extracts, consisting of aromatics and some olefins, should be considered rather as solvents or chemicals for the production of other derivatives of hydrocarbons.

The solvent treatment of gasolines can also be used for the removal of sulphur compounds which are easily soluble in solvents. The sulphur compounds are extracted with aromatic hydrocarbons. Further separation of the sulphur compounds from aromatics, however, is practically impossible. Bataafsche Petroleum Maatschappij [Fr. Pat. 850,532 (1939)] recommends the use of methyl and ethyl sulphonic acids as solvents for selective extraction of sulphur compounds.

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Chapter 7

Cracked Products Other Than Gasoline

Cracked Gases

Gasoline is the main product of cracking, but gas, recycle stock, residuum and coke may be considered as by-products.

Cracked gases are produced in all cracking operations. As has been stated in Chapter 2, the yields of cracked gases depend upon many variables, including the nature of charge, time-temperature factor of cracking, and pressure. The average yield of cracked gases is close to 500 cubic feet per barrel of charge from gas oils, processed in the mixed phase residuum operation with maximum yield of gasoline (about 60-65 per cent). The yields of gases sharply decrease with decreasing yield of gasoline, as the data of Table 172 show.¹⁸

Table 172. Comparative Yields in Cracked Gasolines and Gases.

Cracking Stock	Yield in Cracked Gasoline (% by vol.)	Cu. Ft. of Gas on Barrel of Stock
Ventura crude oil, sp. gr. 0.933	48	368
Same	57.2	542
Spindletop crude oil, sp. gr. 0.882	52.9	264
Same	65.2	438
Spindletop crude oil, sp. gr. 0.919	46.1	334
Same	58.1	608

Vapor-phase cracking produces on an average 1500 cubic feet gas per barrel of charge for a maximum yield of gasoline in the residuum process.

Chemical Composition of Cracked Gases

The chemical composition and properties of cracked gases, obtained in the same process, depend upon the conditions under which the gas is separated. Thus receiver gases differ substantially from stabilizer gases. The receiver gases, or gases directly produced from cracking units, are of low specific gravity and are rich in methane. On the other hand, the properties of the receiver gases depend upon the pressure of condensation. Such units as the Holmes-Manley or Dubbs units which employ high pressure for the condensation of gasolines, give cracked gases of lower specific gravity as compared with the gases of other systems, where condensation takes place under low pressures.

The marked effect of the pressure of condensation upon the chemical composition of cracked gases may be illustrated by some data of Egloff and Morrell,¹¹ given in Table 173.

The cracked gases of high specific gravity (1.3 and up with reference to air) are obtained from the stabilization units as unstable (with regard

Table 173. Chemical Composition of Receiver Cracked Gases vs. Condensation Pressure.
 Charging Stock: Mixture of Fuel Oil, Gas Oil and Wax Distillate.
 Temperature 495°C. (925°F.). Pressure 250 lbs./sq. inch.

Condensation Pressure (lbs./sq. in.)	H ₂	CH ₄ + N ₂	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₄ H ₆
30	0.67	9.4	24.77	2.18	30.68	15.24	7.7	30.68	4.81
250	2.00	64.48	16.06	2.75	6.75	1.90	2.93	6.75	trace

to evaporation losses) constituents of cracked gasolines. They are rich in high molecular weight gaseous hydrocarbons. The average percentage of the stabilizer gas depends on the condensation pressure and is close to 30 to 40 per cent of the total gas produced in cracking.

The difference between the receiver gases from cracking units and the gases from stabilizers is illustrated by the data of Tables 174 and 175 for mixed-phase (Egloff *et al.*¹⁰) and vapor-phase (Holland¹⁵) processes.

Table 174. Chemical Composition of Cracked Gases from M.C. Kerosene Distillate, Produced in Mixed-phase Process.
 Temperature 510°C. (950°F.). Pressure 400 lbs./sq. inch.

	Receiver, 30 lbs./sq. in.	Stabilizer
Hydrogen and Methane	53.0	11.3
Ethane	20.6	18.6
Ethene	4.4	2.2
Propane	8.7	19.5
Propene	7.0	14.5
Butanes	3.1	10.3
Butenes	1.9	7.6
Butadiene		6.9
Heavier	9.1	?

Table 175. Chemical Composition of Cracked Gases from Gulf (Produced in Vapor-phase Cracking.

	Receiver	Stabilizer
Methane and Hydrogen	38.81	11.37
Ethane	13.15	12.35
Ethene	20.31	15.56
Propane	3.68	
Propene	13.15	44.87
Butanes	6.43	13.86
Butenes		
Higher	2.47	1.99

Under the same cracking conditions, the chemical composition of cracked gases depends upon the charging stock to a comparatively small extent. On the contrary, the cracking conditions very strongly affect the chemical composition of gases. High cracking temperature favors the formation of hydrogen and gaseous olefins. A high pressure is favorable to the polymerization of olefins. Thus the gases of vapor-phase cracking are richer in olefins and hydrogen than those of the mixed-phase process. Tables 176 and 177 contain the data on the average chemical composition of cracked gases produced in mixed- and vapor-phase processes.

The average data of Table 176 relate to the modern mixed-phase operation at temperatures of 500°C. (932°F.) or higher. If the tempera-

ture of process is more moderate, the content of olefins is somewhat lower. As has been mentioned above, the content of olefins decreases under high pressures of the process.

Table 176. Average Chemical Composition of Cracked Gases Produced in the Mixed-phase Process.

Specific Gravity (air = 1) from 0.8 to 1.0 per cent by volume.

	Low-pressure condensation about 50 lbs./sq. in.	High-pressure condensation about 200 lbs./sq. in.
Hydrogen	1	3
Methane	40	65
Ethane	16	16
Ethene	3	3
Propane	21	5
Propene	9	4
Butanes	5	2
Butenes	4	2
Heavier	1	
Olefins	16	9

Table 177. Average Chemical Composition of Cracked Gases Produced in the Vapor-phase Process.

Low-pressure condensation.

Specific Gravity (air = 1) from 1.00 to 1.10.

	% by Vol.		% by Vol.
Hydrogen	7	Butanes	2
Methane	30	Butenes	6
Ethane	12	Butadiene	1
Ethene	23	Higher	1
Propane	4	Total Olefins	44
Propene	14		

The composition of cracked gases from the Houdry process (low-pressure condensation) is given by Peterkin *et al.*^{19b} as follows:

Hydrogen	5.4	Isobutane	5.0
Methane	9.4	Isobutene	0.5
Ethane and ethene	6.1	<i>n</i> -Butene	3.3
Propene	6.1	<i>n</i> -Butane	42.9
Propane	20.8	Sp. gr.	1.565

The Houdry gases contain a low percentage of olefins and methane as compared with the cracked gases of thermal cracking.

The content of olefins in the gases of vapor-phase cracking increases with increasing temperature up to a maximum corresponding approximately to 750-800°C. (1382-1572°F.). At still higher temperatures, the decomposition of olefins is considerable, resulting in an increasing content of hydrogen and methane at the expense of olefins. The data of Groll,¹² given in Table 178, clearly show this phenomenon. The time of cracking was the same in all experiments.

It should be noted that the figures of Table 178 are expressed in weight per cents of the charging stock and cannot be directly compared with those of the previous tables.

The chemical composition of cracked gases produced by aromatization

Table 178. Chemical Composition of Cracked Gases in Vapor-phase Cracking of Spray Oil vs. Temperature.

Temperature (°C.)	600	650	700	750	800	850
Yield of gas (% by wt.)	14.2	45.2	52.2	58.5	58.0	52.9
Chemical Composition (% by wt. of cracking stock)						
Hydrogen	0.1	0.3	0.4	0.5	0.7	1.4
Methane	2.2	6.7	10.2	15.9	16.5	19.6
Acetylene	0.0	0.0	0.0	0.0	0.0	0.6
Ethene	4.3	13.0	16.2	21.2	24.6	23.4
Ethane	1.6	3.8	4.3	5.1	4.2	3.2
Propene	3.7	11.2	13.4	11.3	11.3	4.3
Propane	0.4	2.9	1.9	1.6	0.7	0.4
Butenes	1.7	6.4	5.3	2.9	0.0	0.0
Butanes	0.2	0.9	0.9	0.3	0.0	0.0
Total Olefins	9.7	30.6	34.9	35.4	35.9	28.3

of petroleum products is close to the data of Table 178 at 700-800°C. For instance, Dunstan and Howes,⁹ give the following figures for the chemical composition of cracked gases formed in the aromatization of propane and butanes at 750-900°C. (1382°-1472°F.):

Hydrogen	10-25	% by volume
Methane	50-65	" "
Ethene	20-25	" " "
Ethane	0-10	" " "

The following figures illustrate the chemical composition of the gases of the Pintsch process and other processes used for the production of aromatics and gases from petroleum products:

Hydrogen	10-20	% by volume
Methane	30-40	" " "
Ethane	5-15	" " "
Olefins, mostly ethene	20-40	" " "

The analytical data given above include only the content of hydrogen and hydrocarbons which can be considered as normal constituents of cracked gases. The content of "impurities," such as carbon dioxide, carbon monoxide, nitrogen, hydrogen sulphide, is usually small, not exceeding one to two per cent. The content of hydrogen sulphide, however, may be considerably higher, depending upon the nature of the charging stock and amounting to 5-10 per cent for some charging stocks from Mexico, Venezuela and California. The formation of hydrogen sulphide in such large quantities when cracking charging stocks high in sulphur causes bad corrosion of the cracking equipment and requires the use of special alloys or linings of corrosion-resistant alloys, as has been discussed in Chapter 4 (p. 248).

The hydrogenation gases after the removal of hydrogen consist of methane hydrocarbons, including methane, ethane, propane and butanes, and hydrogen sulphide. When charging stocks high in sulphur are hydrogenated, the content of hydrogen sulphide in hydrogenation gases may be high, due to the almost complete transformation of all sulphur compounds into hydrogen sulphide in the presence of high-pressure hydrogen.

A few years ago the cracked gases were considered as waste products

of cracking and were used as the cheapest sort of fuel. The polymerization of gaseous olefins and thermal conversion of hydrocarbon gases into valuable gasolines of high octane number have changed the intrinsic value of cracked gases. The stabilizer cracked gases, containing a large proportion of olefins for polymerization and a large proportion of propane and butanes for thermal conversion, are particularly valuable as charging stocks for the processes in question.

The receiver gases, low in olefins and rich in unconvertible methane and ethane, cannot be processed directly and have to be previously treated with oils or solvents to increase the concentration of convertible hydrocarbons.

As has been stated in Chapter 1, isoölefins, such as isobutene, are particularly valuable with regard to polymerization, producing high-octane fuels, including isoöctane. The chemical composition of the butane-butene fraction of stabilizer gases varies in broad limits. The butane-butene fraction produced from cracked gasolines of the mixed phase process usually contains about 50 per cent of butanes, 35 per cent of normal butene and 15 per cent of isobutene. The content of butanes in the butane-butene fraction may be higher than 50 per cent, but the ratio of normal butene to isobutene remains mostly close to 2:1. The percentage of normal butane usually is considerably higher than that of isobutane.

A typical analysis of the B-B fraction from thermal mixed-phase cracking is given in the following table:

Propane and propene	2 per cent
<i>n</i> -Butane	38 " "
iso-Butane	13 " "
<i>n</i> -Butenes	31 " "
iso-Butene	15 " "
Heavier	1 " "

Snow [U.S.P. 2,128,971 (1938)] gives the following composition for the B-B fraction (mixed-phase cracking):

Iso-Butane	11.4 per cent
<i>n</i> -Butane	49.0 " "
iso-Butene	10.1 " "
Butene—1	10.4 " "
Butene—2	18.2 " "
Butadiene	0.9 " "

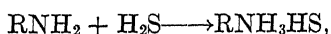
Cracked gases, particularly with a high content of methane and ethane, are widely used for fuel within and outside of refineries. The calorific value of cracked gases depends upon the chemical composition and varies from 11 to 14 cal. per liter, or from 1100 to 1700 B.t.u. per cubic foot.

Purification of Cracked Gases

As has been mentioned, some cracked gases may contain a considerable percentage of hydrogen sulphide. The removal of this undesirable

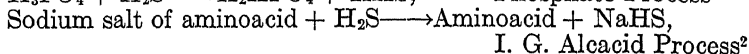
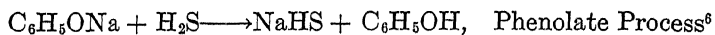
constituent of gases does not involve any difficulties and may easily be carried out by caustic solution. The caustic solution saturated with hydrogen sulphide is a waste product without any commercial value. During recent years new methods of the removal of hydrogen sulphide have been developed which do not form waste products and, moreover, may transform hydrogen sulphide into sulphuric acid or sulphur.

All these processes use either a weak base or a sodium (potassium) salt, formed by a weak acid, for the absorption of hydrogen sulphide. Hydrogen sulphide, absorbed by the reagent, produces a salt of the weak base or sodium (potassium) sulphide. When the reagent has been saturated with hydrogen sulphide, it is decomposed at higher temperatures (about 100°C.), liberating hydrogen sulphide and recovering the initial reagent for repeated use. The process is continuous, the charge of the reagent being circulated between the absorber and reactivator. The following equations represent the reactions involved:



Girbotol Process²⁴

where RNH_2 represents an amine,



I. G. Alcaacid Process²

The processes in question are based on the reversibility of the reactions given above; they take place at low temperatures in the direction of the formation of sulphides and at high temperatures in the reverse direction. Hydrogen sulphide liberated in the reactivator can be either discarded or oxidized to sulphur dioxide and further to sulphuric acid.

The Thylox process¹¹ uses a solution of ammonium salt of sulpho-arsenic acid (5 per cent of arsenic expressed as As_2O_3), which reacts with hydrogen sulphide according to the equation: $(\text{NH}_4)_3\text{AsO}_2\text{S}_2 + \text{H}_2\text{S} \rightarrow (\text{NH}_4)_3\text{AsOS}_3 + \text{H}_2\text{O}$. The reaction is quantitative, and almost all hydrogen sulphide is absorbed by the solution. The regeneration of the spent solution takes place at 45°C. in a stream of air in a special tower: $(\text{NH}_4)_3\text{AsOS}_3 + \frac{1}{2}\text{O}_2 \rightarrow (\text{NH}_4)_3\text{AsO}_2\text{S}_2 + \text{S}$. The regenerated solution is used again after the separation of sulphur. This process directly transforms hydrogen sulphide into sulphur.

Recycle Stocks

The recycle stock is an intermediate product of cracking which is commonly used for repeated cracking or recycling to obtain the maximum yield of gasoline. As has been described above (p. 161), a lighter fraction of recycle stock is frequently withdrawn from cracking units and used for furnace oil.

The recycle stocks are obtained in the fractionating equipment of cracking units, mostly in fractionating and flash towers. The fractionat-

ing towers separate recycle stocks from cracked gasoline or naphtha. The flash towers separate recycle stocks from tar or final residuum which is withdrawn from cracking. Thus the recycle stocks from flash towers are of a higher boiling range and more aromatic than those from fractionating towers.

The boiling range of recycle stocks used for recycling may be different, depending on the general scheme of cracking. In non-selective cracking the boiling range of recycle stock is wide, from 150°C. (302°F.) up to 400°C. (752°F.). Various fractions of the recycle stock may be separated in selective cracking; a lighter recycle fraction, being cracked under more severe conditions, has a comparatively low end point. Table 179 gives some data on the properties of recycle stocks.

Table 179. Properties of Recycle Stocks from M.C. Charging Stock.

Recycle Stock	Specific Gravity at 15°C.	A.P.I. Gravity 60°/60°F.	I.B.P. (°F.)	10% (°F.)	50% (°F.)	90% (°F.)	E.P. (°F.)
Non-selective mixed-phase	0.917	22.8	240	465	550	700	750
Selective mixed-phase							
Naphtha (Reforming)	0.790	47.6	300			460	490
Light	0.893	27.0			450	510	
Heavy	0.934	20.0			560	675	

The boiling range of recycle stocks as marketable products can be made to order in the proper fractionating equipment of cracking units. The recycle stocks, marketed as furnace oils, have a boiling range from 350 to 700°F. according to the specification of these products. Other properties of the recycle stocks, such as specific gravity, aromaticity (aniline point), etc. depend on the cracking conditions and the nature of the charging stocks.

Chemical Composition of Recycle Stocks

The recycle stocks differ very substantially from the straight-run distillates of the same boiling range due to a high content of unsaturates and aromatics. The content of unsaturates in recycle stocks produced in pressure cracking is usually close to 20 per cent and is considerably less than in cracked gasolines. Recycle stocks produced by cracking of paraffin waxes or petrolatum may contain up to 40 per cent of olefins. The content of aromatics in recycle stocks depends upon the charging stock and varies from 10 to 25 per cent or more. The content of aromatics in recycle stocks is greater than in cracked gasolines. Table 180 contains comparative data on the properties of a straight-run distillate and a moderately cracked recycle stock produced from the same mixed base crude.²²

It will be seen from these data that the two distillates are very similar with reference to the boiling range. On the contrary, the difference in chemical composition is very marked. The recycle stock contains a larger percentage of aromatics and particularly of unsaturates, manifested in

high specific gravity, refractive index, iodine number and low aniline point.

Table 180. Properties of Straight-run and Recycle Distillates from Grozny Mixed Base Crude.

	Total Amount Unsat- urates and Aromatics (%)	Sp. Gr. at 15°C.	A.P.I. Gravity	Aniline Point (°C.)	Iodine No.	Refrac- tive Index	
Straight-run	16	0.806	44.1	68.6	0.35	1.4599	
Recycle	36	0.819	41.3	56.4	61.4	1.4677	
-----A.S.T.M. Distillation-----							
	Flash M.P. (°F.)	I.B.P. (°F.)	10% (°F.)	50% (°F.)	90% (°F.)	I.P. (°F.)	Viscosity at 20°C.
Straight-run	144	369	390	439	540	572	0.01847
Recycle	146	378	414	450	538	572	0.01864

Table 181 gives the chemical composition of the recycle stocks boiling from 200-300°C. (392-572°F.). The recycle stocks were treated with fuming sulphuric acid (1 vol. per 1 vol.) for the removal of unsaturates and aromatics. After washing and neutralization, the treated recycle stocks were redistilled up to the end point of the original recycle stocks. The percentage of paraffins and naphthenes was calculated on the basis of aniline points of the treated products.²²

It may be seen from Table 181 that the chemical composition of the recycle stocks gives a very clear reproduction of the character of the original product. Thus paraffin wax produces a recycle oil containing 55-58 per cent paraffins and 11-14 per cent naphthenes, while naphthenic and asphaltic charging stocks give recycle oils containing from 30 to 55 per cent naphthenes.

The large amount of unstable unsaturates present in recycle stocks makes them unstable in storage. In contrast to straight-run distillates, the recycle stocks rapidly lose their color, and dark brown or black gum-like substances settle out from them. Thus 0.9 gram of a gum settled out from 10 liters of a recycle stock after 3 to 4 months. The gum was insoluble in petroleum hydrocarbons, slightly soluble in benzene and easily soluble in chloroform and ethyl alcohol. Other properties of the gum: melting point 140°C., specific gravity at 15°C. 1.043, iodine number 74.6, content of sulphur 1.6 per cent. The gum, similar to the gums produced in cracked gasolines, solidified after further oxidation.

The treatment of a recycle stock of the boiling range 200-300°C. (392-572°F.) with sulphuric acid gave the results summarized in Table 182.

Complete removal of unsaturates takes place only by an excess of strong sulphuric acid. The treatment with an excess of dilute 86-per cent sulphuric acid or with 5-10 per cent by weight of 66°Bé. sulphuric acid removes unsaturates and aromatics only partially as in the case of cracked gasolines. On making an A.S.T.M. distillation of the treated recycle stocks, its final boiling point is always higher than that of the

Table 181. Chemical Composition of Recycle Stocks.

Cracking Stock	Cracking Conditions			Recycle Stock			Chemical Composition			
	Cracking Conditions			Recycle Stock			Aromatic and			
	Temp. (°C.)	Press. (atm.)	Dura- tion (min.)	Before Fuming H ₂ SO ₄ Treatment	After Fuming H ₂ SO ₄ Treatment	Aniline Point (°C.)	Unsatu- rated carbons (%)	Naph- thene Hydro- carbons (%)	Par- affin Hydro- carbons (%)	
Grozny paraffin distillate	400	5	303	Sp. Gr. @ 15°C.	Sp. Gr. @ 15°C.	Aniline Point (°C.)	26	34	40	
Grozny paraffin distillate	425	5	63	0.840	0.795	80.2	32	25	43	
Grozny paraffin distillate	425	10	63	0.831	0.795	82.0	31	32	37	
Paraffin wax	450	10	12	0.838	0.795	79.9	28	14	58	
Paraffin wax	450	10	32	0.782	0.771	85.5	34	11	55	
Medicinal Vaseline oil	450	10	12	0.783	0.773	85.9	45	34	21	
Grozny asphalt base gas oil distillate	450	10	12	0.843	0.810	77.0	40	29	31	
Grozny spindle oil distillate	450	10	12	0.862	0.823	79.6	45	33	22	
Grozny asphalt base engine oil distillate	450	10	12	0.862	0.812	77.3	45	34	21	
Grozny asphalt base cylinder oil distillate	450	10	12	0.850	0.807	77.4	41	35	24	
Grozny asphalt base fuel oil	450	10	12	0.852	0.807	77.7	48	30	22	
Kaluga crude oil	450	10	12	0.868	0.830	71.4	38	55	7	
Baku machine oil	450	10	12	0.849	0.808	77.1	40	37	23	
Grozny mixed base fuel oil	450	10	12	0.833	0.795	82.2	31	25	44	

Table 182. Treatment of Recycle Stock with Sulphuric Acid.

Treatment	Volume Acid (%)	Strength of H_2SO_4 (%)	Sp. Gr. at 15°C.	Viscosity at 20°C.	Refrac- tive Index at 15°C.	Anilin Point (°C.)	Iodine No.
Untreated	..	86	0.820	0.01773	1.4672	56.6	61.16
Treated	10	86	0.819	0.01896	1.4672	58.3	47.38
	100	86	0.820	0.02175	1.4692	59.9	37.76
	200	86	0.820	0.02179	1.4692	60.1	34.88
	300	86	0.820	0.02215	1.4691	60.5	33.64
Same, redistilled up to 300°C. after treatment	100	86	0.814	0.01927	1.4630	60.4	40.01
	200	86	0.814	0.01925	1.4632	60.9	37.30
	300	86	0.814	0.01919	1.4632	61.1	36.98
Treated	5 (by wt.)	93.23	0.820	0.01895	1.4662	58.5	46.42
Same, redistilled up to 300°C.	5 (by wt.)	93.23	0.814	0.01776	1.4648	58.9	46.77
Treated	10 (by wt.)	93.23	0.822	0.01970	1.4674	58.4	45.39
Same, redistilled up to 300°C.	10 (by wt.)	93.23	0.816	0.01776	1.4655	58.7	45.99
Treated	300 (by vol.)	98	0.797	0.02044	1.4502	78.8	
Same, redistilled up to 300°C.	300 (by vol.)	98	0.788	0.01796	1.4476	78.7	0.05

original recycle stock. Thus the formation of high-boiling polymers during the acid treatment takes place as in the case of cracked gasolines. The removal of these polymers formed by redistillation invariably increases the paraffinicity of the treated recycle stock, resulting in decrease in specific gravity and in increase in aniline point.

Use of Recycle Stocks for Furnace Oils

The recycle stocks of suitable boiling range can be used for furnace, Diesel, and illuminating oils. The production of furnace and Diesel oils from recycle stocks is of increasing importance in this country. The production of illuminating oils, unimportant in the United States, may be of commercial interest in the countries which consume large amounts of this product.

The production of furnace oil from recycle stocks largely increases each year due to an increasing consumption of domestic fuel. The high consumption of furnace oil takes place in the winter time when the consumption of motor fuel seasonally declines. Thus the production of furnace oil in cracking becomes an important factor in securing continuous and full-time operation of cracking units.

The use of recycle stocks for furnace oils is simple. The specification requirements of flash point (100°F. or 110°F. min. and 165° or 190°F. max.), pour point (15°F. max.), distillation (maximum end point is 560°F. or 90% point at 600°F.), and carbon residue (0.05 on 10% bottoms) for furnace oils are very close to the properties of recycle stocks of the same end point. The odor, color and stability may easily be improved, if necessary, by sweetening or by light treatment with sulphuric acid followed by neutralization and sweetening. Redistillation after acid treatment and neutralization very markedly improves the properties of furnace oils produced from recycle stocks, particularly color and stability. Redistillation is necessary for less stable recycle oils when a stronger sulphuric acid (93-per cent or more) is used in amounts of 2 lbs. per barrel or more. Brandt and Hougen⁵ recommended the treatment of cracked furnace oils by one per cent of dilute sulphuric acid (25-per cent) and in the second stage by caustic methanol in the absence of air. Caustic

methanol extracts the unstable constituents more efficiently than water caustic. The treatment is performed in the absence of air due to very easy oxidation of the methanol extract and discoloration which is imparted to the treated oil. The method is claimed to eliminate high expenses involved in the redistillation of furnace oils in the conventional method of treatment.

Use of Recycle Stocks for Diesel Oils

The production of Diesel oils from recycle stocks meets difficulties with regard to cetane numbers, or Diesel indices. The cetane number means the percentage of cetane in a reference fuel containing this hydrocarbon and α -methyl naphthalene, which has the same ignition qualities as the fuel being investigated. The Diesel index is closely related to the cetane number and is calculated from aniline point and A.P.I. gravity of fuels according to the equation:

$$\text{Diesel Index No.} = \frac{\text{Aniline Point, (}^{\circ}\text{F.)} \times \text{Gravity A.P.I.}}{100}$$

Kreulen^{16a} gives a very simple approximate relationship between the cetene numbers of straight-run gas oils and their chemical composition:

$$\text{Cetene No.} = -0.2A + 0.1N + 0.85P.$$

in which A , N and P represent respectively the percentage of aromatic rings, naphthenic rings and paraffinic side chains determined by the ring analysis method. The cetene numbers are determined with cetene and α -methylnaphthalene as reference fuels and are somewhat greater (approximately 15 per cent) than cetane numbers. This equation shows a very close relationship between cetene numbers and paraffinicity of gas oils.

Cracking, which increases the octane number of cracked gasolines in comparison with straight-run products, has the reverse effect on the cetane or cetene numbers of gas oils. A cracked gas oil has a lower cetane number than the straight-run gas oil from the same crude. The negative effect of cracking on the cetane numbers is due to the increased content of olefins and aromatics in cracked products. As a result, the paraffinicity and cetane numbers of cracked gas oils are lower than those of straight-run oils produced from the same crude.

Hubner and Murphy¹⁸ give the following average cetane numbers for straight-run and cracked Diesel fuels of the same origin (Table 183). The average boiling range of the Diesel fuels is from 300 to 700°F.

The cetane numbers of the cracked fuels of Table 183 are not quite comparable due to variations in the extent of cracking. For instance, the cracked oils from Michigan and W. Texas crudes were evidently obtained under much more severe cracking conditions than in the case of other cracked oils.

The cetane numbers, or Diesel indices, of cracked fuels may be improved by suitable treatment. Treatment with sulphuric acid removing

Table 183. Cetane Numbers of Straight-run and Cracked Diesel Fuels.

Origin	Straight-run Diesel Fuel		Cracked Diesel Fuel	
	A.P.I. Gravity	Cetane No.	A.P.I. Gravity	Cetane No
Pennsylvania	42.4	62	34.9	48
Michigan	43.5	68	22.4	37
Kentucky	37.5	52	34.9	48
E. Texas	38.0	55	30.2	40
W. Texas	34.6	45	23.1	30
Gulf Coast	35.6	58	32.6	41
Oklahoma	37.9	56	31.4	35
Rocky Mountain	36.2	59	28.6	43
California	35.5	47	28.2	32

part of the olefins and aromatics increases the paraffinicity and Diesel index numbers, as will be seen from the data of Woods²⁵ given in Table 184.

Table 184. Acid Treatment of Cracked Diesel Fuels.

Acid (lbs./bbl.)	0	10	50
Treating loss (%)	0	6	27
Diesel index No.	45	48	55
Pour Point (°F.)	-25	-25	-10

The figures of Table 184 show that a considerable amount of sulphuric acid is required to produce an appreciable increase in Diesel index, *i.e.*, from 45 to 55. The consumption of sulphuric acid and treating losses are too high for commercial applications of this method of treatment.

The solvent treatment of cracked Diesel fuels seems to be much more promising from the commercial standpoint. The same author studied the solvent treatment of cracked fuels by sulphur dioxide and found that the Diesel index numbers may be increased by 30 units depending upon the volume ratio of solvent to cracked fuel and yields of refined oil. The same solvent was used by Steffen and Saegbarth.²³ The Diesel index of a cracked oil was improved from 40 to 62 and 81.

Dryer, Chenicek, Egloff, and Morrell⁸ made an extensive study of the solvent extraction of Diesel fuels. The cracked gas oil fractions in the boiling range from 330-410°F. to 610-690°F. of various origin were treated by sulphur dioxide and furfural in continuous operation. Sulphur dioxide is more selective than furfural. The effect of the solvent treatment on the properties of Diesel fuels may be illustrated by the following data for a California cracked Diesel fuel (Table 185).

Solvent extraction improves cetane numbers of raffinates without appreciable change in distillation curve, viscosity and flash point. A low cetane number California cracked fuel produces 75 per cent refined fuel with the improvement in 15 cetane units. The yields of 50-55 cetane number Diesel fuel from Pennsylvania and Mid-continent cracked fuels amounts to 80 per cent. The properties of solvent extracts are given in Table 186.

The flash points and A.S.T.M. distillation of the solvent extracts are approximately the same as those of the initial cracked fuels. The extracts

Table 185. Properties of Raffinates from California Cracked Diesel Fuel.

Ratio, solvent/solution	Furfural as Solvent				Sulphur Dioxide as Solvent		
	0.	0.45	0.9	1.5	0.25	0.5	1.0
Raffinate (%)	100	87	81	78	85	78	75
Gravity (A.P.I.)	30.7	32.6	34.7	34.9	32.6	34.6	36.0
Aniline point (°F.)	111.6	125.1	133.2	134.6	122.4	135.7	143.6
Flash point (°F.)	190	180	180	178	180	175	180
Pour point (°F.)	< -35	-35	-25	-30	-35	-25	-25
Viscosity at 100°F. (sec.)	35.2	35	35	35	35	35	35
Total sulphur (%)	0.45	0.33	0.27	0.24	0.34	0.25	0.20
Conradson carbon (%)	0.06	0.03	0.03	0.03	0.02	0.02	0.01
A.S.T.M. distillation (°F.), I.B.P.	409	395	402	393	412	411	410
10%	435	433	430	427	437	438	436
50%	471	471	466	467	472	475	474
96%	561	560	559	562	565	568	566
E.P.	633	644	628	639	631	638	640
Cetane number	33	37	42	42	37	44	48

Table 186. Properties of Solvent Extracts from California Cracked Diesel Fuels.

Ratio, solvent/solution	Furfural as Solvent				Sulphur Dioxide as Solvent		
	0	0.45	0.9	1.5	0.25	0.5	1.0
Extract (%)	0	13	19	22	15	22	25
Gravity (A.P.I.)	30.7	15.5	15.6	15.5	18.7	17.5	17.4
Aniline point (°F.)	111.6	-8	-23	-11	-6	-15	-30
Octane blending value			80	80	75	80	81
Pour point (°F.)	< -35		< -35	< -35		< -35	
Viscosity at 100° (sec.)	35.2		36.2	36.5		35.0	
Total sulphur (%)	0.45		1.21	1.41			
Conradson carbon (%)	0.06		0.04	0.10		0.27	

are very aromatic and can successfully be used for tractor fuels or for cracking charging stocks for producing aromatic high-octane number gasolines. The elimination of losses and the total recovery of raffinate and extract is an unquestionable advantage of the solvent treatment.

The use of light recycle stocks for illuminating oils meets the same difficulties as in the case of Diesel oils. In contrast to straight-run kerosenes, recycle stocks of the same boiling range are very difficult to treat with sulphuric acid, if a satisfactory color must be obtained. The illuminating properties of treated and redistilled light recycle stocks are close, or slightly inferior, to those of straight-run kerosenes. The consumption of sulphuric acid is from 6 to 10 lbs. per barrel for recycle stocks of proper distillation range produced from paraffin or mixed-base cracking crudes.

Solvent refining seems to be a more adequate method for the production of illuminating oils from recycle stocks. The raffinates obtained by Dryer *et al.* from cracked fuels are too heavy with regard to the fractional composition to be used for illuminating oils. Satisfactory illuminating oils might probably be produced under the same conditions of treatment from the cracked distillates of a lighter fractional composition.

The instability of recycle stocks used for Diesel fuels also may be objectionable. In addition to gum formation in storage, the injection system of Diesel engines is covered by a sticky substance when unstable recycle stocks are used as fuel. Treatment with sulphuric acid and redistillation, as well as solvent treatment make recycle stocks stable with respect to gum formation. Hydrogenation of recycle stocks for the production of Diesel fuels may be carried out under the conditions specified in Chapter 3. The effect of hydrogenation on cetane numbers has been discussed in the same chapter.

Light recycle stocks boiling between 300 and 550°F. may be successfully used for tractor fuels. Barger^{2a} gives the following characteristics of cracked tractor fuels:

A.P.I. Gravity at 60°F.	Color Saybolt	Octane Number	Sulphur (%)	Copper Dish Gum per 100 cc.
30.1	Darker -16	33	0.213	
32.0	" "	43	0.280	2100
37.8	" "	39	0.176	766

The straight-run tractor fuels of the same boiling range have a better color, a lower sulphur content and less gum formation, but are badly detonating (octane number from -7 to 12).

As has been stated in Chapter 3, hydrogenation recycle stocks are almost completely saturated and stable. They can be used for furnace oils, Diesel oils, etc. without any treatment.

High-boiling Cracked Distillates

The cracked distillates used for recycle stocks commonly have a maximum end point of about 400°C. (752°F.) or lower. The heavier cracked distillates cannot successfully be cracked due to excessive coke formation, and are withdrawn from the cracking units in cracked residues. The properties of the distillates produced from cracked residues depend upon the nature of the charging stock and, particularly, upon the cracking conditions. The aromaticity of the distillates progresses with increasing temperature-time factor of cracking.

The properties of high-boiling cracked distillates versus cracking conditions were studied by Sachanen and Bestougeff.²¹ A Balachany fuel oil of specific gravity 0.908 was cracked at 425°C. (797°F.) and 15 atmospheres' pressure. The duration of cracking varied within a wide range, from 30 minutes to 6 hours. The results are given in Table 187.

Table 187. Cracking Balachany Fuel.
Cracking Temperature 425°C. (797°F.), Pressure 15 atm.

Time	Gas + Loss	Gasoline up to 392°F.	Recycle Stock 392-572°F.	Residuum	Coke
32 min.	5.1	12.2	21.1	61.6	0.0
1 hour 32 "	6.7	28.6	23.4	41.0	0.3
3 " 02 "	11.3	36.8	22.0	28.6	1.3
6 " 02 "	14.7	52.3	13.1	7.9	12.0

The residues obtained were distilled in high vacuum, and the boiling temperatures under vacuum were converted to atmospheric pressure according to the equation of Ramsay and Young and the boiling curve of normal octane.¹³ The results of distillation and the properties of fractions are given in Tables 188-191.

Chemical Composition of High-boiling Cracked Distillates

The progressive change in the chemical composition of cracked distillates versus time of cracking is first noticed in the specific gravity. In

Table 188. Vacuum Distillation Cracked Residuum From Balachany Fuel Oil. Duration of Cracking 32 Minutes.

The cracked residuum had a specific gravity of 0.927, pour point below -20°C ., flash point 184°C ., Saybolt viscosity 240 at 122°F .
The residuum amounts to 61.6 per cent of the original fuel oil.

Fraction No.	—Boiling Temperature—			% Over	Sp. Gr. at 15°C .	Pour Test ($^{\circ}\text{C}$.)	Flash Point ($^{\circ}\text{C}$.)	Saybolt Viscosity at 122°F .
	Atmospheric Pressure ($^{\circ}\text{C}$.)	During Distillation ($^{\circ}\text{C}$.)	Mercury Pressure (mm.)					
1	290-339	142-178	11	9.1	0.882	below -20	143	41
2	339-366	178-205	11.0-14	7.6	0.891	below -20	159	48
3	366-394	205-226	14	8.0	0.897	-15	176	58
4	394-408	226-239	14	8.3	0.904	-5.5	191	70
5	408-427	239-248	15.5-13	7.6	0.913	+2	205	96
6	427-449	248-267	13-14	7.4	0.918	7	216	144
7	449-474	267-288	14-15	7.6	0.924	9	228	235
8	474-492	288-303	15-16	7.5	0.928	15	237	330
9	492-536	303-325	16	7.7	0.930	21	270	550
Bottoms				27.3	0.979			fluid
Losses				1.9				

Table 189. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil. Duration of Cracking 1 Hour, 32 Minutes.

The cracked residuum had a specific gravity of 0.966, pour point below -20°C ., flash point 167°C ., Saybolt viscosity 280 at 122°F .
The residuum amounts to 41 per cent of the original fuel oil.

Fraction No.	—Boiling Temperature—			% Over	Sp. Gr. at 15°C .	Pour Test ($^{\circ}\text{C}$.)	Flash Point ($^{\circ}\text{C}$.)	Saybolt Viscosity at 122°F .
	Atmospheric Pressure ($^{\circ}\text{C}$.)	During Distillation ($^{\circ}\text{C}$.)	Mercury Pressure (mm.)					
1	297-336	142.5-170.5	9	8.4	0.896	below -20	137	40
2	336-361	170.5-189	9	8.0	0.903	-20	151	44
3	361-378	189-202	9	7.7	0.911	-14	164	50
4	378-386	202-236	9-20	8.4	0.923	-6	177	61
5	386-400	236-248	20	7.4	0.934	-0.5	191	76
6	400-432	248-248	20	7.8	0.941	+2	205	100
7	432-451	248-262	11.5	7.7	0.948	+12	217	165
8	451-480	262-282	11.5-11	7.9	0.958	+18	231	325
9	480-519	282-310	11-10.5	7.4	0.970	+20	246	680
10	519-551	310-332	10.5-10	7.7	0.984	+18	257	126 At 212°F .
Bottoms				19.9	1.11			
Losses				1.6				

Table 190. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil. Duration of Cracking 3 Hours and 2 Minutes. The cracked residuum had a specific gravity of 1.018, pour point of $-13^{\circ}\text{C}.$, flash point of $168^{\circ}\text{C}.$, Saybolt viscosity 605 at $122^{\circ}\text{F}.$ The residuum amounted to 28.7 per cent of the original fuel oil.

Fraction No.	—Boiling Temperature—			Mercury Pressure (mm.)	% Over	Sp. Gr. at $15^{\circ}\text{C}.$	Pour Test ($^{\circ}\text{C}.$)	Flash Point ($^{\circ}\text{C}.$)	Saybolt Viscosity at $122^{\circ}\text{F}.$
	At Atmospheric Pressure ($^{\circ}\text{C}.$)	During Distillation ($^{\circ}\text{C}.$)	At						
1	311-338	150-169	8	-7	8.5	0.920	below		
2	338-358	169-180	7	-6.5	8.2	0.932	-20	136	37
3	358-376	180-192	6.5		8.1	0.959	-16	159	44
4	376-392	192-203	6.5		8.8	0.959	-14	171	52
5	392-413	203-218	6.5		8.0	0.969	-7	180	60
6	413-435	218-233	6.5		8.0	0.969	+3	191	80
7	435-470	233-256	6.5-6		7.7	0.980	+9	202	130
8	470-524	256-295	6.0		7.8	0.995	+14	215	285
9	524-568	295-326	6.0		7.7	1.02	+20	231	78 } At
10	568-588	326-340	6.0		8.1	1.05	+10	246	172 } $212^{\circ}\text{F}.$
Bottoms					6.6	1.08			*
Losses					20.0	1.19			†
					0.5				

* Semi-solid, melting point by Kremer-Sarnow $26^{\circ}\text{C}.$

† Semi-solid, melting point by Kremer-Sarnow $155^{\circ}\text{C}.$

Table 191. Vacuum Distillation of Cracked Residuum from Balachany Fuel Oil. Duration of Cracking 6 Hours and 2 Minutes. The cracked residuum had a specific gravity of 1.12. The residuum amounted to 7.9 of the original fuel oil.

Fraction No.	—Boiling Temperature—			Mercury Pressure (mm.)	% Over	Sp. Gr. at $15^{\circ}\text{C}.$	Pour Test ($^{\circ}\text{C}.$)	Saybolt Viscosity at $122^{\circ}\text{F}.$
	At Atmospheric Pressure ($^{\circ}\text{C}.$)	During Distillation ($^{\circ}\text{C}.$)	At					
1 and 2	280-354	139-194	13		16.5	0.995		40
3 and 4	354-416	194-235	13	-11	21.5	1.058		64
5 and 6	416-546	235-329	11	-10.5	18.3	1.11	separation of crystals	
7 and 8	546-554	329-343	10.5-13		14.3	1.14	separation of crystals	
Bottoms					29.1	1.23		solid
Losses					0.3			

addition to high specific gravity, the heavy cracked fractions become less viscous. However, the properties of cracked fractions in the first three experiments (time from 32 minutes to 3 hours 2 minutes) remain to a certain degree similar to those of straight-run distillates. Under the most severe conditions employed (6 hours 2 minutes), the cracked fractions completely lose their petroleum character. They consist mostly of solid aromatic hydrocarbons. A more complete information on the hydrocarbons in high-boiling cracked distillates was obtained as a result of further investigation. Tables 192 and 193 give the data on the molecular weight, ultimate analysis and average formulas of the fractions corresponding to Tables 190 and 191, *i.e.*, to the cracking conditions 3 hours and 6 hours at 425°C. The molecular weights were determined in benzene solutions. In the calculations of formulas the content of oxygen was not taken into consideration due to the comparatively small amount present in the fractions.

The aromatization of hydrocarbons is almost complete after cracking under more severe conditions. For instance, the chemical composition of cracked oils obtained after even three hours' cracking of Balachany fuel oil corresponds to that of aromatic hydrocarbons, and only the lighter gas oil fractions can contain hydroaromatic compounds which are derivatives of Tetralin. The dehydrogenation of naphthenes is very easily carried out and is completed before the hydrocarbon has lost all its side chains, due to the fact that after the long chains have been split up, the splitting up of short chains, particularly those of methyl groups, is carried out with more difficulty.

The crystalline fractions obtained after 6 hours' cracking are purely aromatic. The larger part of the crystals separated in one of the fractions had a melting point of 201°C., which is close to the melting point of 202 to 203°C. for 1,3-dimethylantracene. Analysis of the crystals revealed the composition to be 93.10 per cent carbon and 6.66 per cent hydrogen, as compared with 93.16 per cent and 6.84 per cent of carbon and hydrogen, respectively, in dimethylantracene.

The small amount of fractions left after the investigation did not permit a more complete investigation of the solid compounds present. Therefore only their melting points could be determined after twice recrystallizing from alcohol. Due to the fact that most of the crystals obtained were probably a mixture of isomers, their melting temperatures between 190 and 230°C. could be of only informational value. The ultimate analysis and the melting points indicate that these crystalline hydrocarbons are composed principally of substituted anthracenes.

The liquid aromatic fractions are apparently the derivatives of naphthalene, diphenyl and other bicyclic hydrocarbons. The non-alkylated naphthalene and diphenyl can sometimes be detected in the high-boiling cracked distillates in very small quantities.

An investigation of the chemical composition of cracked oils may throw some light on the composition of high-boiling crude oil fractions,

Table 192. Molecular Weights, Ultimate Analysis and Formulas of Cracked Fractions Obtained in Cracking at 425°C. (797°F.) for 3 Hours, 2 Minutes.

No. of Fraction	Boiling Temp. (°C.)	Sp. Gr. at 15°C.	Molecular Weight	Ultimate Analysis		Formula	Series
				Hydrogen	Carbon		
1	311-338	0.920	211				
2	338-358	0.932	229	11.62	88.30	C ₁₇ H ₂₆	C _n H _{2n-3}
3	358-376	0.959	245				
4	376-392	0.959	260	11.04	88.09	C ₁₉ H ₂₈	C _n H _{2n-10}
5	392-413	0.969	246				
6	413-435	0.980	289	10.64	88.98	C ₂₂ H ₃₀	C _n H _{2n-10}
7	435-470	0.995	298				
8	470-524	1.02	317	9.62	88.68	C ₂₃ H ₃₀	C _n H _{2n-16}
9	524-568	1.05	370	9.59	89.74	C ₂₃ H ₃₆	C _n H _{2n-20}
10	568-588	1.08	370				

Table 193. Molecular Weights, Ultimate Analysis and Formulas of Cracked Fractions Obtained in Cracking at 425°C. (797°F.) for 6 Hours, 2 Minutes.

No. of Fraction	Boiling Temp. (°C.)	Sp. Gr. at 15°C.	Molecular Weight	Ultimate Analysis		Formula	Series
				Hydrogen	Carbon		
1-2	280-354	0.995	199	9.36	90.28	C ₁₅ H ₁₈	C _n H _{2n-12}
3-4	354-416	1.058	220	7.94	91.50	C ₁₇ H ₁₈	C _n H _{2n-16}
5-6	416-546	1.11	252	7.17	91.15	C ₁₉ H ₁₈	C _n H _{2n-20}
7-8	546-554	1.14	294	6.85	92.29	C ₂₃ H ₂₀	C _n H _{2n-26}

due to the fact that the structure of the oil molecule is simplified, hydrogen and side chains being lost while the basic ring structure remains, which makes it possible to determine the nature of the compounds. It is understood, however, that the cracking conditions should be mild enough to prevent the formation of cyclic hydrocarbons as a result of various condensations of unsaturates discussed in Chapter 1.

Table 194. Vacuum Distillation of Cross Cracked Residuum from
Mid-Continent Gas Oil.*

No. of Fraction	% by Vol.	Temp. (°F.)	Gravity A.P.I.	Flash Point (°F.)	Pour Point (°F.)	Viscosity at 100°F. 210°F.	Aniline Point (°F.)
Res.	100			250	25	55	
1	10	100-240	24.0	150	-30	35.2	54.3
2	10	240-275	20.5	235	0	41.4	57.0
3	10	275-315	18.2	295	20	53.0	57.5
4	10	315-345	15.6	315	45	74.4	65.8
5	10	345-390	14.1	350	65	39.8	100.7
6	10	390-450	13.3	410	85	49.0	
7	10	450-490	13.3	445	100	64.8	
Bottoms	30						

* The pressure was 2 mm. Hg. for all.

Orlov, Protyanova and Flegontov¹⁹ studied the chemical composition of a residuum from high-temperature cracking of liquid petroleum products at 700-800°C. (1292-1472°F.). The following compounds were isolated: naphthalene, α - and β -methylnaphthalene, mixture of dimethylnaphthalenes, acenaphthene, anthracene and phenanthrene. Corresponding to the high temperature of the process, the residuum contained a considerable amount of non-alkylated aromatic hydrocarbons, as products of complete dealkylation and dehydrogenation.

The heavy distillates of commercial cracked residues closely correspond to those of Tables 189 and 190, or to the temperature-time factors 425°C. (797°F.), 92 minutes, and 425°C., 182 minutes. The specific gravities and aromaticity of the distillates may be higher or lower, depending upon the charging stock. Table 194 contains the data on the distillates of a Cross residuum.

The content of unsaturates and aromatics absorbed by concentrated sulphuric acid is about 50 per cent for the first five fractions and about 70 per cent for the last two fractions.

The degree of aromatization of cracked fractions of the Cross-cracked residuum is close to that of the above experiment at 425°C. (797°F.), 3 hours and 2 minutes (Table 190).

The heavy distillates of reforming or vapor-phase-cracked residues are highly aromatic due to the drastic cracking conditions of the processes.

Use of High-boiling Cracked Distillates

As the data of Tables 188-190 and 194 show, some high-boiling distillates of cracked residues produced in the mixed-phase process are comparatively viscous. Beard⁴ distilled cracked residues in high vacuum and treated viscous fractions with sulphur dioxide. Lubricating oils may be produced by this method.

A Cross-cracked residuum of the following characteristics:

Gravity, A.P.I.	12.8°
Viscosity, Saybolt Furoi	19
I.B.P.	331°F.
70 per cent over at	705°F.

distilled in high vacuum, produced viscous fractions between 56 and 80 per cent over. The properties of these fractions are as follows:

Gravity, A.P.I.	10.3°
Flash, O.C.	445°F.
Pour Point	35°F.
Viscosity at 100°F., Sayb.	1032
" " 130°F., "	343
" " 210°F., "	65
Viscosity Index	-12
Color	Dark Green
Conradson Carbon	1.56%
Sulphur	0.79%

These fractions were treated with sulphur dioxide four times in batch operation, producing 40 per cent of a refined oil. After dewaxing, the lubricating oil had the following properties:

Gravity, A.P.I.	20.5°
Flash, O.C.	435°F.
Pour Point	5°F.
Viscosity at 100°F., Sayb.	380
" " 130°F., "	167
" " 210°F., "	53
Viscosity Index	66
Color	Light 6
Conradson Carbon	0.20%
Sulphur	0.45%
Viscosity-gravity const.	0.885

Osterstrom^{19a} produces highly aromatic lubricating oils from the cracked residuum of high-temperature vapor-phase cracking at temperatures of 1000 to 1300°F. No data on the yields and properties of these oils are available (with an exception of viscosity approximately of 200 to 600 Saybolt seconds at 140-100°F.). The claim on the high viscosity index of the oils in question seems to be in contradiction to the low viscosity index properties of polycyclic aromatic hydrocarbons with short side chains.

The paraffinic side chains of lubricating oils produced from cracked residues are short. The cyclic hydrocarbons of these lubricants are polyaromatic due to dehydrogenation. As a result, the viscosity index and stability are poor, unless the treatment is very drastic, resulting in small yields.

Tropsch *et al.*^{23a} investigated chlorination of cracked residues by chlorine and sulphuryl chloride. In both cases the main reaction is substitution. Chlorine reacts with residues until from 30 to 40 grams of chlorine have been absorbed by 100 grams of residue. The chlorination product can react with benzene in the presence of aluminum chloride;

yielding viscous oils of a better viscosity index than that of the initial residue.

The heavy cracked distillates, being predominantly aromatic, react with sulphuric acid with formation of sulphonic acids. Two volumes of 66°Bé. sulphuric acid are sufficient to convert quantitatively all aromatic hydrocarbons present in cracked distillates into sulphonic acids which are dissolved in acid sludge. The effect of 98-per cent sulphuric acid upon cracked distillates is shown in Table 195.

Table 195. Effect of 98-Per Cent Sulphuric Acid on Cracked Distillates.

Stock Treated	—Specific Gravity of Stock—		% Sulphonatable
	Before Treatment	After Treatment	
Fraction No. 1, Table 189	0.995	0.910	75
Fraction No. 2, Table 189	1.06		87

The properties of the sulphonic acids and sulphonates depend upon the molecular weight and cyclic structure of treated fractions. MacLaren¹⁷ described the sulphonation of cracked distillates, pressure tar distillates, etc., boiling above 450°F., by fuming sulphuric acid, from 1 to 8 lbs. of acid per gallon of distillate. The yields of sulphonated compounds are reported to be 55 per cent and more of the distillate treated.

The sulphonic acids produced from cracked products can be converted into phenolic substances by the reaction between sodium sulphonates and potassium and sodium hydroxides. The phenolic derivatives formed are efficient oxidation inhibitors which can be used in cracked gasolines and lubricating oils [Sachanen and Waldo, U.S.P. 2,161,317 (1939)]. *

Cracked Residues

The cracked residues consist of the highly condensed hydrocarbons and other derivatives formed in cracking, which are removed from cracking units as by-products of the process. They are stripped from lighter fractions in evaporators or flash chambers.

As by-products, the cracked residues are of considerable importance, being produced in about the same yield as cracked gasolines. The following figures illustrate the output of cracked gasoline and residues in the United States during the last three years:

	1937	1938	1939
Cracked gasoline (bbls.)*	268,136,000	270,471,000	295,142,000
Cracked residue (bbls.)*	235,739,000	252,245,000	260,441,000

* Including distillate fuels.

The separation of cracked residues from light fractions in conventional evaporators is not complete, and, as a result, the cracked residues from evaporators contain a large proportion of light distillates. The flashing in flashing chambers is accompanied by some fractionation, resulting in the formation of heavy and high-boiling residues. The properties of cracked residues, such as specific gravity, viscosity, initial boiling point, depend largely upon the effectiveness of flashing.

The following data illustrate the relative amount of low-boiling frac-

tions in cracked residues obtained in evaporators without flashing (Table 196). Thus the cracked residuum contains 30 per cent of light recycle stock. The total proportion of gas oil to be stripped in the flash chamber may be as great as 50-60 per cent, as in the case of the cracked residuum of Table 194.

Table 196. Distillation of Cross-Cracked Residuum from Evaporator (A.P.I. Gravity 12.2).

Fraction	%	Temp. (°F.)	A.P.I. Gravity	Saybolt Viscosity at 100°F.
1	10	-480	26.4	34.2
2	10	480-527	21.7	36.4
3	10	527-581	20.3	41.2

The cracked residues from flashing chambers are of high specific gravity and contain less recycle stock. The properties of flashed cracked residues from the mixed-phase process are summarized in Table 197. The residues in this table are obtained with the maximum yield of cracked gasoline, *i.e.*, about 60-65 per cent from gas oils and correspondingly less from topped crudes. The content of free carbon may be greater than that given in Table 197, depending upon the performance of the cracking coil.

Table 197. Average Properties of Cracked Residues Produced in Flashing Chambers.

Charging Stock	Gas Oil	Topped Crude
A.P.I. Gravity, 60°F./60°F.	4-10	0-10
Flash, Pensky-Martens (°F.)	200-250	200-250
Viscosity (Saybolt)		
Furol Seconds at 122°F.	20-100	100-1000
Univ. Seconds at 210°F.	50-80	100-300
Distillation		
I.B.P. (°F.)		450
10 per cent		600-700
30 per cent		750-800
50 per cent		850-900
Carbon (insoluble in benzene) (%)	0.1	0.1-0.5
Asphaltenes (%)	2-10	5-20

The viscosity of cracked residues is low in comparison with that of straight-run residues after the removal of lubricating distillates, particularly from naphthenic and asphaltic crudes. It is due, evidently, to the viscosity breaking, *i.e.*, to the cracking of high molecular weight viscous hydrocarbons.

The pour point is not characteristic of the cracked residues on account of the very high viscosity of many cracked residues at low temperatures. It varies on an average from 0 to 100°F. The content of sulphur varies within broad limits depending upon the charging stock. It may be as high as 5 per cent for cracked residues from some Mexican crudes, 1-2 per cent for California cracked residues and only 0.5 per cent for Mid-continent cracked residues.

When kerosene distillates are cracked or naphthas are reformed, the cracked residues are lighter in respect to the fractional composition.

Table 198 gives the data on a cracked residuum from reforming a West Texas naphtha.

Table 198. Properties of Cracked Residuum Produced in Reforming of West Texas Naphtha.

A.P.I. Gravity	7.0
Viscosity Saybolt at 100°F.	110.0
Flash (°F.)	205
I.B.P.	402
10 per cent	440
50 " "	458
90 " "	521
E.P.	601

The cyclic hydrocarbons of cracked residues are thermally unstable and are decomposed with formation of coke and gas. The distillation of cracked residues is accompanied by total decomposition of residues at temperatures close to 750-800°F., as shown in Table 199. The calorific or heating value of cracked residues depends upon the specific or A.P.I. gravity, as can be seen from Table 200.

Table 199. Distillation of Cracked Residues.
Cracked Residue from Gas Oil, 16.8 A.P.I. Gravity.

% by Volume	Temperature (°F.)
10	493
20	525
30	556
40	590
50	622
60	666
70	711
80	747
90	743
92½	694
Coke 9.33% by weight	

Cracked Residue from Panuco Crude Oil, Sp. Gr. 1.018.

% by Volume	Temperature (°F.)
10	538
20	613
30	655
40	691
50	725
60	741
70	716
Coke 22.6% by weight	

Table 200. Average Heating Values of Cracked Residues.

A.P.I. Gravity at 60°F.	High Heating Value		Net Heating Value	
	Cal./Kilogram	Btu./lb.	Cal./Kilogram	Btu./lb.
15	10,750	18,600	9,800	17,600
10	10,200	18,300	9,700	17,400
5	9,900	17,800	9,400	17,000

The high heating values correspond to the laboratory determinations of the combustion heat in a bomb with total condensation of water at 60°F. The net heating values correspond to the heat of combustion, when

the products of combustion are cooled to 60°F. without condensation of water. The figures given above relate to the ash and water-free cracked residues.

Structure of Cracked Residues

The cracked residues consist mostly of polycyclic aromatic hydrocarbons formed as a result of the aromatization and condensation processes described in Chapters 1 and 2. In addition to aromatic hydrocarbons, asphaltic materials, such as resins and asphaltenes, frequently with a high content of oxygen and sulphur, are present in cracked residues in considerable quantities. The formation of the asphaltic compounds is due to the same condensation processes involving oxygen and sulphur compounds of the charging stock. Neutral resins are dissolved in hydrocarbons and asphaltenes are colloiddally dispersed, being peptized by heavy aromatic hydrocarbons and resins. The coke, formed in cracking, is also concentrated in cracked residues in the form of heterogeneous particles of various size. The heterogeneity of cracked residues containing coke can easily be detected under a microscope.

The non-homogeneity of cracked residues, as well as asphalts, may also be detected by the so-called Oliensis spot test that is carried out as follows. A residuum (or asphalt) is dissolved in the naphtha of boiling range between 300 and 410°F., with 50 per cent over between 335 and 355°F. A.P.I. gravity of the naphtha should be 49 to 50 and aniline point 138 to 145°F. For the test 2 cc. of cracked residuum, or an equivalent weight of asphalt, is placed in a 25-cc. Erlenmeyer flask and dissolved in 10.2 cc. of the naphtha. If necessary, the flask is immersed in a bath of boiling water. The contents of the flask are swirled by hand. When the dispersion is complete, the flask is cooled to room temperature. A drop of the solution is then placed on filter paper. In the case of cracked residues and asphalts, the drop forms a dark annular nucleus surrounded by a brown circular stain. In the case of straight-run products, the drop usually is homogeneous without the dark nucleus.

Coke or carboids in cracked residues are determined by solution of the residuum in an excess of benzene. One volume of residuum is dissolved in 20-30 volumes of benzene. The carbon or coke insoluble in benzene is separated by filtration, washed with benzene, dried at 110°C. and weighed.

The determination of asphaltenes and carboids in cracked residues is carried out by precipitation with an excess of petroleum ether (boiling range from 30 to 60°C.). One volume of the residuum is blended with 40 volumes of the petroleum ether. The coagulation lasts about 24 hours. Then the asphaltenes and carboids precipitated are separated by filtration, washed with petroleum ether, dried at 110°C. and weighed.

Batchelder and Wellman³ showed that the asphaltenes of cracked residues are less soluble in cyclohexane than those of straight-run residues. A method of differentiating between straight-run and cracked residues has been developed on the basis of this property. The difference between

the cyclohexane- and benzene-insoluble contents of straight-run residues is essentially zero. The per cent cyclohexane-insoluble less benzene-insoluble can be used as an index of the content of asphaltenes of cracked residues.

In addition to asphaltenes, the content of carbenes, *i.e.*, asphaltenes insoluble in carbon tetrachloride, is frequently determined by the same operation as in the case of asphaltenes, petroleum ether being replaced by carbon tetrachloride. All these tests are also made for cracked asphalts. Straight-run residues contain only traces of carbenes. Thus Hillman and Barnett^{14a} suggested using the content of carbon tetrachloride-insolubles as a measure of the percentage of cracked residuum in a blended fuel.

Storage Stability of Cracked Residues

The content of free carbon or coke in cracked residues may be as high as one per cent or more. Such residues are very unstable in storage, gradually precipitating coke in the form of a thick sludge on the bottom of tanks or on the heater coils located in the tanks. The modern cracking units, however, produce cracked residues with a smaller amount of coke, not exceeding 0.1-0.2 per cent, due to better control of the coke-forming processes.

The precipitation of carbonaceous sludge in storage of cracked residues may be due to coagulation of the asphaltenes. The asphaltenes, and especially the carbenes, present in cracked residues differ from those in straight-run products in a lesser stability toward coagulation. As a result, the cracked residues are not completely homogeneous even in the absence of coke. On the other hand, it should be emphasized that there is no definite border line between coke insoluble in benzene and asphaltenes soluble in it.

The dispersion of asphaltenes and carboids in cracked residues is closely connected with the adsorption of neutral resins and high molecular weight cyclic hydrocarbons by the particles of asphaltenes and carboids. The neutral resins and cyclic hydrocarbons of high molecular weight form a protective layer on the surface of the colloid particles and prevent the coagulation. This phenomenon predetermines the behavior of cracked residues in storage. Blending cracked residues with straight-run distillates invariably deteriorates the sludging properties of cracked residues. The low molecular weight paraffin and naphthene hydrocarbons of straight-run distillates partially extract the protective layers on the colloid particles and favor coagulation and sludging.

The aromaticity or aniline point of blended gas oils is very important to the final result of blending, as has been shown by Batchelder.³ A virgin gas oil of aniline point 154°F. admixed with a cracked residuum strongly increased the carbonaceous deposit on heaters; a cracked gas oil of aniline point 104.5°F. increased to a much less extent; another gas oil of aniline

point 68°F. did not affect the deposition of carbon; and a solvent extract of aniline point 31°F. markedly lessened the carbon deposition.

The blending of cracked residues with straight-run residues of low specific gravity may give the negative effect and increase the deposition of carbonaceous material. On the other hand, the addition of straight-run asphalts to cracked residues stabilizes the latter due to increase in the concentration of resins and high molecular weight hydrocarbons. Various cracked residues can be blended without any appreciable effect on the sludging.

The methods of the artificial precipitation and removal of coke from cracked residues, such as treatment in the electric field of high voltage or precipitation with sulphuric acid, are not used commercially to any large extent.

Cracked Asphalts

Cracked residues can be transformed into cracked asphalts by further stripping lighter distillates, as well as by oxidation. The stripping is performed in commercial practice either by steam or in high vacuum. The cracked residues of high specific gravity become asphaltic after the removal of approximately 50 per cent distillates. This operation concentrates neutral resins and asphaltenes in the bottoms to the extent required for the asphaltization of the product. The oxidation of cracked residues by air at 270-300°C. (518-572°F.) produces neutral resins and asphaltenes as a result of oxidation.

The vacuum flashing of cracked residues may be directly connected with the cracking plant. The hot-cracked residuum at a temperature of 350-400°C. (662-752°F.) enters the insulated flashing tower under a pressure of about 50 mm. Superheated steam is introduced in the bottom of the tower for stripping. Vacuum is maintained by the steam ejector. Under these conditions the distillates are readily flashed from the asphalt without additional heating. Various specifications of road oils and asphalts may be produced by this method controlled by the percentage of overhead distillates.

The following data give an idea on the content of neutral resins and asphaltenes in the cracked asphalts.²² An asphalt base gas oil was cracked, yielding 28 per cent of cracked residuum of specific gravity 0.970 (14.3 A.P.I.). The cracked residuum was stripped in high vacuum from light fractions, producing 31 per cent cracked asphalt of the properties given in Table 201.

The properties of cracked asphalts from the same charging stock depend upon the temperature-time factor of cracking. The relative content of asphaltenes increases with increasing cracking, resulting in higher softening points of asphalts. Table 202 represents the data relating to the asphalts produced from Balachany fuel oil at various durations of cracking at 425°C. (797°F.). The asphalts were formed by stripping in high vacuum to the same final temperature.

Table 201. Properties of Cracked Asphalt, Produced from Cracked Residuum of 0.970 Specific Gravity.

Specific gravity at 15°C.	1.12
Softening point by Kraemer-Sarnow, °C.	49
Ductility at 25°C. (cm.)	63.3
Penetration at 25°C.	7
Composition (% by weight)	
Carbon (free)	6.1
Asphaltenes	21.1
Resins	12.1
Oils	63.3

The properties of cracked asphalts are very close to those of straight-run products. Hausman¹⁴ compared straight-run and cracked asphalts of the same melting points produced from the same Rumanian crude. The Dubbs-cracked residuum of specific gravity 1.005 and viscosity 250 at 212°F. was blown with steam until the proper consistency of asphalt was obtained. Table 203 gives the comparative properties of cracked and straight-run asphalts.

Table 202. Properties of Cracked Asphalts.

Duration of Cracking	—425°C., 15 atm.—			
	32 min.	1 hr. and 32 min.	3 hrs. and 2 min.	6 hrs. and 2 min.
Sp. gr. at 15°C.	0.979	1.11	1.19	1.23
Softening point (Kraemer-Sarnow) (°C.)	semi-fluid	76	155	170
Asphaltenes (%)	6.3	30.6	58.3	about 70
Resins (%)	24.1	28.0	18.1	...
Oils (%)	71.6	43.6	25.3	...

Table 203. Comparison of Straight-run and Cracked Asphalts.

Property	M.P. 91.4°F.		M.P. 104°F.		M.P. 122°F.	
	Cracked	Str. Run	Cracked	Str. Run	Cracked	Str. Run
Sp. gr. at 15°C.	1.055	1.017	1.065	1.024	1.079	1.035
Melting point (°F.) (Kraemer-Sarnow)	91.4	91.4	104	104	122	122
Ductility at 15°C.	100	100	100	100	18	16
Ductility at 25°C.	100	31				
Penetration at 25°C.	137	102	51	42	16	19
Fixed carbon (%)	15.9	15.5	19.7	16.3	21.8	18.1
Ash content (%)	0.50	0.41	0.25	0.42	0.35	0.45
Solubility in CS ₂ (%)	99.07	99.57	98.80	99.53	98.75	99.51

Cracked asphalts of the same melting point are of higher specific gravity than straight-run products due to a higher aromaticity. The penetration values are fairly close. The solubility in carbon disulphide as well as in benzene is appreciably higher for straight-run products. The proportion of the part insoluble in carbon disulphide is less than 0.5 per cent for the straight-run asphalts and more than 1 per cent for the cracked asphalts, due to coke formation in cracking.

The method of manufacture of cracked asphalts, steam (vacuum) distillation or blowing with air, does not affect appreciably the properties of cracked asphalts. The same author gives the following data for two asphalts produced from the same flashed residue (Table 204).

The production of cracked asphalts is not confined to naphthenic and asphaltic crudes as in the case of straight-run asphalts. The cracked asphalts can be produced by reduction or oxidation of cracked residues

Table 204. Properties of Air-blown and Steam-blown Cracked Asphalts.

Property	Air-blown	Steam-blown
Sp. gr. at 25°C.	1.056	1.068
Penetration at 25°C. (mm.)	106	99
Volatility at 450°F. (%)	0.57	0.34
Penetration of residue at 25°C.	94.5	89.5
Ductility at 15°C. (cm.)	125	125
“ at 25°C. (cm.)	125	125
Flow point (°C.)		
Flow test at 50°C.	5 min. 58 sec.	10 min. 59 sec.
Flash point in open cup (°C.)	199	216
Fixed carbon (%)	16.71	14.32
Solubility in CS ₂ (%)	99.63	99.54
Solubility in CCl ₄ (%)	93.60	92.15

from naphthenic and paraffinic crudes, as well as from gas oils. The asphaltic constituents are formed in the process of cracking as condensation products. The cracked asphalts described by Hausmann were produced from a semi-paraffinic reduced crude cracked in a Dubbs unit. A Russian refinery produces a cracked asphalt having specific gravity of 1.05 to 1.10, a penetration of 10 to 20 and a ductility above 100, from the Jenkins cracked residuum of specific gravity 0.995. About 60 per cent of distillates are removed by steam distillation. The charging stock for the Jenkins units is a heavy gas oil from a paraffinic crude.

The cracked asphalts are less homogeneous than the straight-run products due to the presence of carboids and asphaltenes which coagulate more easily than those of straight-run products. The non-homogeneity of the cracked asphalts may easily be detected by the Oliensis spot test previously described. Another test is the solubility of asphalts in benzene (or carbon disulphide) or carbon tetrachloride. The cracked asphalts frequently yield a comparatively large proportion of asphaltenes (carbenes) insoluble in carbon tetrachloride and from 0.1 to many per cents of carbon insoluble in benzene (or carbon disulphide).

As in the case of cracked residues, the homogeneity of cracked asphalts may be improved by the addition of some highly aromatic materials which stabilize the colloidal particles present in asphalts. Dengler, Gardner and Felder⁷ claim that the mixing of cracked asphalts with an air-blown uncracked asphaltic residue increases the homogeneity of the asphalts. For instance, equal parts of a cracked residuum of specific gravity 1.065 and of an uncracked residuum from Mexican crude with a softening point of 102°F. were blended, resulting in an increase in solubility in carbon tetrachloride from 94 per cent for the cracked residuum to 99.6 per cent for the blend. The product, by blowing with air or by reducing with steam, gave high-quality asphalts. The poor solubility (90 per cent) of cracked asphalts in carbon tetrachloride may be increased to 99.8 per cent by this method of stabilization with air-blown uncracked residues.

An appreciable content of carbon, insoluble in benzene or carbon disulphide, was a serious drawback to the use of cracked asphalts. At present the content of free carbon in cracked residues as well as in cracked

asphalts, is reduced to a very small figure, as has been previously mentioned.

Coke

Coke is a by-product of the non-residuum cracking process. The yields of coke in the non-residuum process vary from 55 to 120 per barrel of charging stock depending upon the A.P.I. gravity of the latter (page 163). Coke may also be obtained in reaction chambers of cracking units in the residuum process but in comparatively small relative amounts.

The cracking coke is the final product of the condensation processes in cracking. It consists probably of highly polycyclic aromatic hydrocarbons very poor in hydrogen. The temperature of coke formation in the coking and reaction chambers is moderate, not exceeding 450°C. (892°F.). External heating is not used for the coking and reaction chambers. As a result, the cracking coke contains a considerable amount of "volatile" matter, and the content of fixed carbon in cracked coke is comparatively low, 80 to 85 per cent. The proportion of volatiles is between 10 and 15 per cent. In addition, the coke contains ash from 0.1 to 2 per cent and sulphur from 0.1 to 4 per cent. The apparent density of coke changes from 0.6 to 1.0 depending on the temperature conditions of the process. The heating value of cracking coke is from 15,300 to 16,000 B.t.u. per lb. (8,500 to 8,900 Cal. per kg.). Further cracking of coke at high temperatures up to 800°C. (1472°F.) decomposes more and more the hydrocarbons of coke, producing "volatile" matter as decomposition products.

The coke from aromatization or gasification of petroleum products at high temperatures up to 800°C. (1472°F.) substantially differs from the cracking coke. It is similar to common coke and contains much less volatile matter, under 5 per cent, and 95 per cent or more of fixed carbon.

The temperature conditions of coke formation in stills heated externally are more severe than in cracking units. The still coke contains about 10 per cent of volatiles. The coke produced in the Knowles ovens has a low content of volatiles, not exceeding 5 per cent, due to the high temperature of the process. According to Albright,¹ the coke from Knowles ovens contained 97.85 per cent fixed carbon, 1.15 per cent volatiles and 1 per cent ash.

Cracking coke is mostly used for fuel. It cannot be employed as metallurgical coke due to the lack of the mechanical strength and an excess of volatiles. A serious drawback to the use of cracking coke for fuel is its insufficient strength, resulting in high yields of dust and breeze. Binding with tars and briquetting may overcome these difficulties and is sometimes done in practice. The breeze coke may be pulverized and consumed as fuel, particularly in refineries.

Certain sorts of cracking coke, having a low content of ash and sulphur, are used for electrodes, particularly for the aluminum industry. A Russian refinery manufactures this type of coke from the special air-

blown asphalts poor in ash and sulphur. The air-blown asphalts are employed to increase the yield of coke up to 30-35 per cent by weight with reference to the asphalt.

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